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Volume 2. Removal Technology Evaluation

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16. ABSTRACT

The report reviews the methods used to remove sources of sulfur, nitrogen, and trace element pollutants from coal, coal liquids, petroleum, tar sand oils, and shale oils. The evaluation is restricted to systems that remove contaminants before combustion. The survey identifies contaminant removal methods which were used successfully in the past, are used now, or which, although previously unsuccessful, might be used successfully today. The evaluations generally indicate that no single method is effective for removing all of the contaminants from the fuels under consideration, yet permitting the fuel to be recovered unaltered in form and quality. Some methods release the contaminants but the actual removal requires additional processing. Combined processes might offer advantages to overcome the limitations of single-function processes.

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FUEL CONTAMINANTS

VOLUME 2. REMOVAL TECHNOLOGY EVALUATION

by

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ABSTRACT

Volume II of this two-volume report reviews the methods used for the removal of sources of sulfur, nitrogen, and trace element pollutants in fuels characterized in Volume I. This evaluation is limited to those systems which use as their approach the removal of contaminants before combustion. The survey identifies contaminant-removal methods which have been successfully used in the past and/or are currently being utilized. The survey included reviews of techniques which were previously unsuccessful but in today's world might be. The nature of the removal processes, what they achieved, and how it achieved the removal are analyzed.

The methods used for the removal of contaminants from coal, coal liquids, petroleum, tar sand oils, and shale oils are considered and evaluated. The methods are grouped into generalized categories typical of each fuel. For coal, the categories are methods based on physical differences, pyrolysis, liquefaction, chemical refining, and gasification. For the liquid fuels, the categories are based on physical differences, hydrotreatment, chemical refining, pyrolysis processes, and gasification.

From these evaluations it is generally concluded that no single method is effective for removing all of the contaminants from the fuels under consideration and still recover the fuel unaltered in form or quality. Coal liquefaction followed by hydrotreatment and coal gasification release the contaminants in coal, but the actual removal of the contaminant requires additional process steps. For the liquid fuels, hydrotreating and gasification are also found to be the most effective methods of contaminant removal. Combined processes such as chemical refining followed by coal liquefaction might be used to overcome the limitations of single function type processes used for coal.

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1.0 INTRODUCTION

1.1 Technical Objectives

The overall objective of this study is to identify by means of a literature survey possible future environmental control techniques for potential pollutants in solid and liquid fuels which use as their approach the removal of such contaminants from the fuels before combustion. The program included a survey and subsequent evaluation of techniques both past and present plus evaluation of potential new and unique techniques based on detailed basic studies of the fuel-contaminant chemistry and potential removal mechanisms that may be applicable to fuels. Primary emphasis is on the removal of sulfur and nitrogen, but removal of other contaminants such as trace elements and their compounds which are potential pollutants of interest or concern are also considered. These include, but are not limited to, the following: Hg, Be, Cd, As, Pb, Cu, V, Ni, Se, Mn, Sn, F, Cl, Ga, Co, Cr, Ge, Te, B, Br, Mo, Zn, Zr, and P.

1.2 Approach

The approach used to fulfill these objectives was to identify through a literature survey the chemical and physical characteristics of general groups of contaminants and specific contaminants and the problems of removing such contaminants from fuels. (The findings from this part of the study are reported in the first volume on fuel contaminant chemistry.) In addition, the survey was to identify contaminant-removal methods which have been successfully used in the past and/or are currently being utilized and also to look at techniques which were previously unsuccessful but in today's world might be. The nature of the removal process, what it achieved and how it achieved the removal were analyzed. This volume of the report lists, discusses, and systematically categorizes the methods of removal according to the particular contaminants characterized in the first volume of this report and the mechanism for their removal. In some cases major unsuccessful removal methods are also discussed in the light of why they were being investigated and why they were not successful or not implemented.

The approach used to report the findings of the literature survey was to consider methods for the removal of contaminants used for coal, petroleum, tar sand oils and shale oils. The methods have been grouped into generalized categories typical of each fuel. For example, for coal the categories are methods based on physical differences, pyrolysis, liquefaction, chemical refining and gasification while for the liquid fuels the categories are methods based on physical differences, hydrotreatment, chemical refining, pyrolysis processes, and gasification.

2.0 METHODS OF CONTAMINANT REMOVAL FROM COAL

The contaminants in coal have been characterized into the broad categories of pyritic and other inorganic sulfur, organic sulfur, organic nitrogen, and numerous trace elements and their compounds. Methods used for removing all or part of these contaminants in coal prior to combustion fall into five broad categories, based on the processes employed, i.e., physical methods, pyrolysis, liquefaction, chemical refining, and gasification. In the case of physical methods, the intent of the method may be primarily contaminant removal. In another case, such as liquefaction, the contaminant removal occurs as a consequence of the conversion process.

2.1 Physical Methods

The capability of physical methods used to remove contaminants from coal is limited to the removal of those contaminants known to be present as discrete phases that are separatable from the organic portion of coal. Therefore, the physical methods are not expected to remove the sulfur or the nitrogen that is present in the coal structure as organic-sulfur or organic-nitrogen compounds. The physical methods employed in coal-beneficiation operations are primarily designed for the removal of the clay, shale, sand, and pyritic sulfur. Since the pyritic sulfur often comprises a major part of the total sulfur in coal, its removal would significantly reduce the coal sulfur content. Any sulfate-sulfur due to pyrite weathering or gypsum is considered to be present in minor amounts and would be partially removed along with the other mineral matter removed during physical coal-beneficiation operations.

These physical methods are not expected to remove the trace elements Ge, Be, and B known to be associated with the organic portion of coal. Only a small portion of the trace elements P, Ga, Ti, V, and Sb, which are more closely associated with organic material rather than with the mineral matter in raw coal, would be expected to be removed by physical beneficiation methods. Those elements typically associated with the mineral sulfides and carbonates but also found in the organic material would be expected to be partially rejected by the physical methods of contaminant removal (i.e., Co, Ni, Cr, Se, and Cu). Finally, the trace elements Hg, Zn, Cr, Cd, As, Pb, Mo, and Mn, which are closely associated with mineral matter, would be expected to be reduced significantly by physical beneficiation processes. The level of fluorine, which is present as part of the mineral apatite, would also be reduced. The chlorine and bromine contaminants (as well as the sodium and potassium associated with them) which are commonly present as the mineral halite would be removed along with other mineral matter removed during coal beneficiation.

2.1.1 Basic Principles Involved in Physical Methods of Contaminant Removal

In processes using physical methods for the removal of contaminants, the fundamental steps involved are (1) size reduction; and (2) separation of coal from unwanted materials in the crushed or pulverized coal by differences in size, specific gravity, surface behavior, magnetic and electrostatic properties, and other physical differences that are either inherent or induced. The literature is replete in the description of processes and concepts that would optimize both of these steps for maximum recovery of an acceptably clean coal. Several excellent reviews have been compiled on the subject.(1-5) In early citations, the methods had as their purpose the development of processes for rejection of ash-forming constituents and fine-size coal. Later these processes were modified to improve coal recovery, to further reduce the sulfur content, and to produce a uniform end product. Additional modifications and innovations are being developed to cope with the removal of greater amounts of mineral matter and the handling of fine coal produced by mechanized mining of progressively lower quality coals (i.e., higher in ash and sulfur). Because of variations in the nature and quantity of both removable and unremovable impurities, each coal has individual cleaning characteristics.(1)

The basic principles involved in size reduction and the separations based on these physical differences are summarized below. Specific data on contaminant removal based on these physical differences are given in sections discussing the method.

2.1.2 Size Reduction and Screening

Comminution of coal is done to gain access to the coarse and finely disseminated mineral matter in coal, especially that part of the mineral matter and pyrite intimately dispersed in the organic portion of the coal. Crushing and grinding (pulverizing) systems have been developed to match the type of raw coal being processed to the desired clean-coal characteristics. Studies in controlled size reductions are few, but results suggest such approaches can enhance pyritic sulfur removal. Screening is employed to separate the crushed coal into various size fractions resulting from comminution. Some refuse rejection has been demonstrated in conjunction with size reduction and screening studies. In the past, the primary purpose of the screening was to separate the crushed coal into various marketable size fractions that were suited for feeding separation processes described later. In addition, screening provides a means of recovering fines in the original coal feed and those produced during processing operations. Today coal is no longer graded by coal size for marketing purposes. For electric power stations the coal is finely crushed at the point of utilization. For these reasons, coal sizing is now used only when necessary to obtain maximum recovery in the coal preparation plant.(3)

Separation by Gravity Differences. A measure of the amenability of a coal to be "cleaned" by differences in the specific gravities of the coal and refuse is established in the laboratory by washability tests or float-sink evaluation of various grind consists of the coal. Theoretically, the organic constituents of coal with a specific-gravity range of 1.2 to 1.8 could be separated from the mineral matter that consists of material with specific gravities of about 2.65 (clay, shale, sand) and 4.9 (pyrites) by the selection of a liquid with an intermediate gravity.(1-5) The clean coal should float while the refuse should sink in a medium with an intermediate specific gravity. However, total disaggregation of the coal and mineral to their ultimate particles is impossible, and intermediate gravities exist in coal (carbonaceous shale ranges from 2.0 to 2.6). In coal preparation and cleaning facilities, liquid with a specific gravity of about 1.6 is commonly used and this is the value often used in laboratory washability studies to determine the potential of a coal to be cleaned by the float-sink principle. An estimate of the difficulty of the separation of coal from refuse in a plant operation can be made from the amount of material that is present at nearly the same gravity as the separation media.(2) The generalization is as follows:

Amount of Near-Gravity Material	Estimate of Problems in Cleaning Plant
0-7 percent	Simple
10-15 percent	Difficult
20-25 percent	Very Difficult

The efficiency of any process based on the gravity separation method is often evaluated on the basis of laboratory washability data; however, because of the large number of variables involved in the process, these efficiencies can be considered only as a measure of how closely full-scale operations approach these laboratory values. These variables include the characteristics of the coal to be cleaned, the particular method of operation, the amount and nature of the impurities to be removed, the percentage of near-gravity material, the friability of the coal, and the size range being processed.(2) The actual method of separation used will vary with the top size of the coal fraction being processed. Processes based on the use of air classification rather than aqueous or other liquid media are also evaluated by a criteria of performance based on laboratory washability data.

Separation by Differences in Surface Behavior. The surface-property differences between coal and the contaminants it contains can be used to effect their separation. Differences in wetting characteristics, surface charge retention, colloidal (absorbed) surface characteristics, and potential for distribution in immiscible solvents have been employed to remove contaminants from coal, or vice versa.

Although surfacial properties of coal and pyrite do not differ greatly, various schemes employing froth flotation have been used to separate pyrites from finely divided coal and are now considered one of the conventional methods for upgrading coal.(3) Flotation is normally classed as a physical separation method; however, it involves both physical and surface chemical aspects and depends on the selective adhesion of air to some solids. Such solids exhibit nonpolar surface structure and are hydrophobic. They adhere to the surface of fine air bubbles introduced below the surface and are carried to the surface where they are collected as a froth. The process usually involves the use of suitable reagents to establish a hydrophobic surface on the solids to be floated and to render the other solids hydrophylic so that they remain in water suspension. The coal, as for almost any mineral-beneficiation process employing froth flotation, must be finely divided with a top size of 28 mesh (0.6 mm).(3)

Similar surface-property differences are the basis for the separation of one or more components in coal by the use of immiscible liquid systems. In such a system, coal (and other hydrophobic materials) selectively migrates to the water-immiscible phase (oil) or to the interface between the oil and water. With suitable dispersion, coal forms agglomerates while the hydrophylic mineral contaminants remain in aqueous suspension. In selective flocculation, the principle is to selectively aggregate particles of one surface characteristic into flocs while maintaining other species fully dispersed. The flocs can then be separated by some conventional means such as sedimentation or similar gravity methods.

Separation of finely divided material by electrophoresis relies on differences in the surface charge and the mobility of charged particles in aqueous solution suspension. Under the influence of a dc electric field, materials will migrate to the electrode opposite the hydrated surface charge (zeta potential) to effect separation.

When the separation is done in air rather than in solution at substantially higher dc voltages, separation occurs through charge differences on the surface of the particle induced by the electric field. Repulsion from and attraction to the charged electrodes provide a means of separation based on the electrostatic charge carried by the surface of the coal and mineral matter.

Magnetic Separation. Magnetic methods for the removal of impurities from coal appear to be most effective for removal of ferromagnetic and some paramagnetic minerals. Important factors are the liberation size of coal impurities and the development of adequate magnetic susceptability of the impurities prior to separation. Various methods have been reported that achieve the conversion to ferromagnetic forms which allows use of low-intensit magnetic fields for practical and efficient separation. Without pretreatment, very high intensity magnetic fiels are used. The separation method is suited to upgrading finely divided coals (typically minus 48 to 200 mesh or 297 to 74 microns).

2.1.3 Effect of Size Reduction

In a study for the Environmental Protection Agency, the U.S. Bureau of Mines has evaluated the effect of size reduction on the potential for rejection of ash-forming constituents and pyritic sulfur by specific gravity separations (washability studies).(6) The amount of refuse and pyrite that potentially could be removed was dependent on the amount of coal to be recovered. In a study on coals from the Northern Appalachian Region, the reduction of pyritic sulfur, for coals crushed to a top size of 3/8-inch, ranged from 56 percent at a 90 percent clean-coal yield to 76 percent at a 60 percent clean-coal yield. Finer grinding provided greater reductions. These coals, on the average, contained 2.01 percent pyritic sulfur, 3.01 percent total sulfur, and 12,693 Btu per pound. Crushing these coals from a top size of 1-1/2 inches to 14-mesh top size (1.19 mm) and removing the 1.6-specific-gravity sink material gave a product analyzing 0.66 percent pyritic sulfur and 1.66 percent total sulfur with a 92.1 percent Btu recovery. The data in Table 1 were obtained from the work reported by Deurbrouck(6,7) and cover specific coal-bed characteristics, average regional values, and average of the coals studied. The trends observed for the 322* coals studied in the effect of size reduction on pyritic and total sulfur and ash rejection are shown in Figures 1a, 1b, and 1c. Only 30 percent of the coals studied had the potential of being beneficiated to a total sulfur content of 1 percent or less, while more than one-half have the potential for removal of ~50 percent of their total sulfur content. There are noted regional variations. In a similar evaluation of

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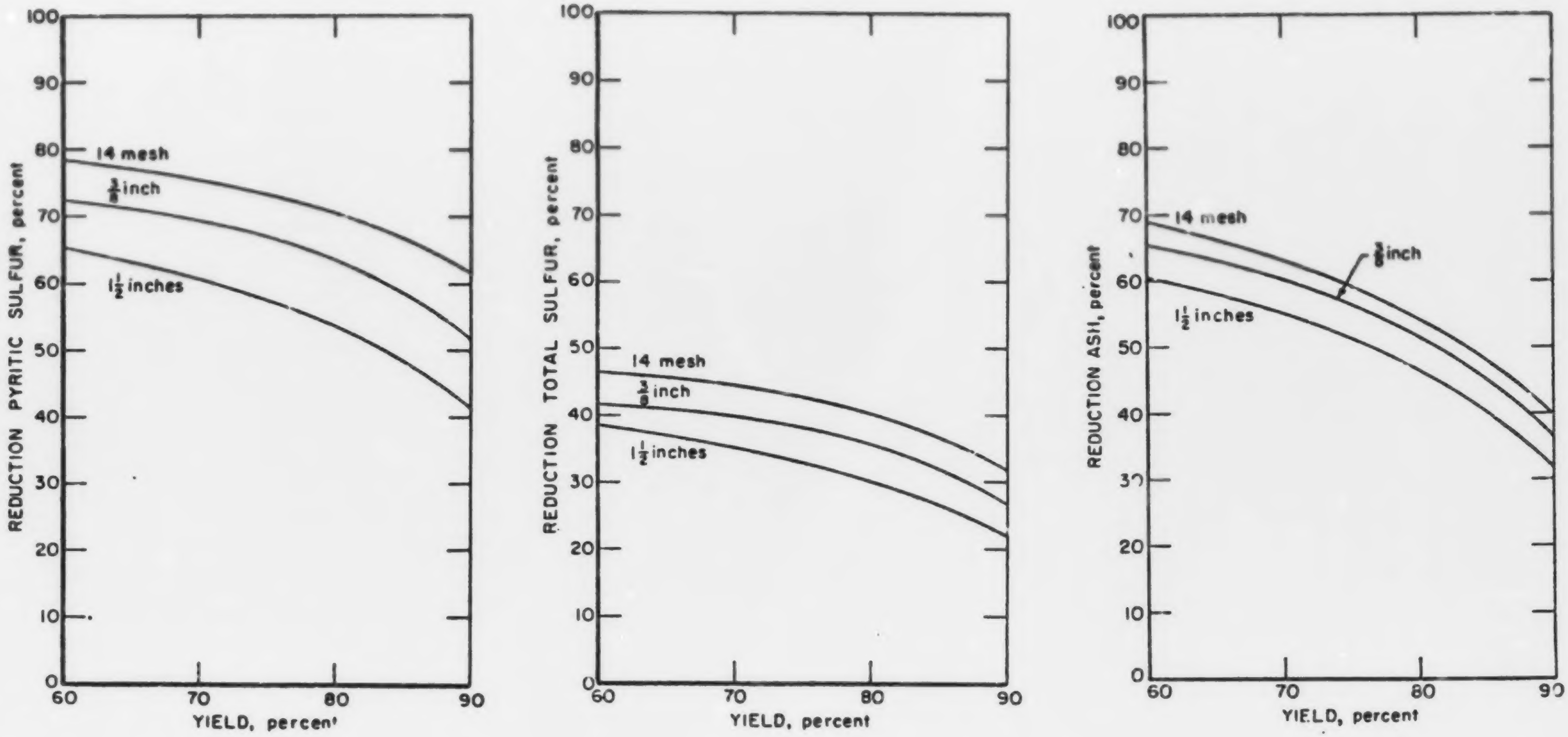
* Now greater than 400 coals.

TABLE 1. POTENTIAL FOR SULFUR REMOVAL OF VARIOUS COALS BY SIZE REDUCTION AND GRAVITY SEPARATION: WASHABILITY ANALYSIS(6,7)
(Top Size 14 Mesh)

Coal Type or Bed	Raw Coal Feed			Sp. Gravity of Separation	Clean Coal			Btu Recovery, percent	Pyrite Reduction, percent
	Sulfur, %		Ash, %		Sulfur, %		Ash, %		
	Pyritic	Total			Pyritic	Total			
Lower Freeport Bed	1.72	2.45	12.9	1.40	0.18	0.83	4.3	86.7	92
Lower Freeport Bed	1.72	2.45	12.9	1.60	0.28	0.94	5.5	94.4	87
Upper Kittanning Bed	1.65	2.23	17.0	1.40	0.12	0.57	4.9	80.7	94
Midwest U.S. Region (Avg)	2.29	3.92	14.1	1.40	-	-	-	-	68
Northern Appalachian Region (Avg)	2.01	3.01	-	1.60	0.66	1.66	-	92.1	65
Average of Study	1.91	3.02	14.0	1.40	0.50	1.69	5.0	79.6	69



(a) Pyritic Sulfur

(b) Total Sulfur

(c) Ash

FIGURE 1. EFFECT OF CRUSHING TO 1-1/2-INCH, 3/8-INCH, and 14-MESH TOP SIZES ON THE LIBERATION OF PYRITIC SULFUR, TOTAL SULFUR, AND ASH.(6))

Results are for the average of 322 coals studied.

Illinois coals, the finer size coal had the potential for greater pyritic sulfur and ash removal than coals crushed to coarser top sizes (1-1/2 inch and 3/8 inch versus 14 mesh).(8) In both studies it was observed that about 69 percent of the pyritic sulfur present in the raw coal had the potential for removal in the finest grind at about an 80 percent coal recovery. Although it is apparent that more contaminants can be removed with finer size coal, the extent of size reduction is limited by the added difficulties (and cost) inherent with processing a finer coal.

The effect of staged crushing and fine grinding of some selected high-sulfur coals on the potential for sulfur removal has been reported.(9) The results from these studies are significant because the study evaluated a coal that was ground to a final top size of 200 mesh. The organic sulfur in this coal was 1.44 percent and the total sulfur of the raw coal was 4.0 percent. The results are shown in Table 2. By crushing in stages to 3/8 inch, 14 mesh, 30 mesh, and finally 200 mesh, a reduction to 1.80 percent sulfur was obtained but the yield was only 42.2 percent. At a yield of 77.5 percent (float at 1.6 sp gr), the sulfur was reduced to 1.96 percent, which is a marked improvement over that obtained for a top size of 14 mesh (3.21 percent sulfur; 78.8 percent yield). Although similar data on all important coal beds were not available, the conclusion based on the study was that the final sulfur content cannot approach the levels attributable to organic sulfur unless the coal is pulverized to at least minus 200 mesh.

Differences in the grinding characteristics of pyrite and coal have been demonstrated.(10,11) Coal can be ground to 70 percent minus 200 mesh in one-seventh the time required for pyrites. Therefore, pulverizing raw coal in a manner that minimizes pyrite grinding, i.e., staged grinding, would make subsequent separations of pyrite easier. The results of the study on the rate of size reduction are given in Figure 2. For coals in which the pyrite is present primarily as finely disseminated material closely associated with the coal (i.e., micron size), this generality may not hold; however, to effect release of such small size pyrite from coal, pulverization would be necessary. In a study related to pyrite separation by means of an air classifier, it was found that for many coals much of the pyrite grains fall into a size range of 250 to 70 microns (60 to 200 mesh) when coal is

TABLE 2. EFFECT ON SULFUR REDUCTION BY STAGED CRUSHING OF RUN-OF-MINE COAL[9] - FLOAT AND SINK ANALYSES[a]

Specific Gravity Fractions	To 1-1/2" x 0 Cumulative		To 3/8" x 0 Cumulative		To 14 Mesh x 0 Cumulative		To 30 Mesh x 0 Cumulative		To 200 Mesh x 0 Cumulative	
	Yield, %	Sulfur, %	Yield, %	Sulfur, %	Yield, %	Sulfur, %	Yield, %	Sulfur, %	Yield, %	Sulfur, %
Float- 1.30	23.4	2.50	29.7	2.41	38.3	2.24	42.8	1.90	42.2	1.80
1.30 - 1.35	60.0	3.15	62.5	3.03	57.5	2.52	59.5	2.00	56.5	1.82
1.35 - 1.40	71.2	3.49	70.5	3.31	67.1	2.75	67.0	2.10	63.5	1.85
1.40 - 1.50	75.0	3.80	78.0	3.65	71.0	3.05	73.5	2.25	75.0	1.94
1.50 - 1.60	82.4	3.90	80.5	3.78	78.8	3.21	77.4	2.31	77.5	1.96
Sink + 1.60	100.0	4.08	100.0	4.14	100.0	4.01	100.0	4.04	100.0	4.02

(a) Pittsburg Bed, Panhandle District 6, West Virginia. Deep mine coal; head ash 20.0 percent; total sulfur 4.01 to 4.14.

Forms of Sulfur:	Sulfate	Organic	Pyritic
Percent, Moisture Free	0.02	1.44	2.59

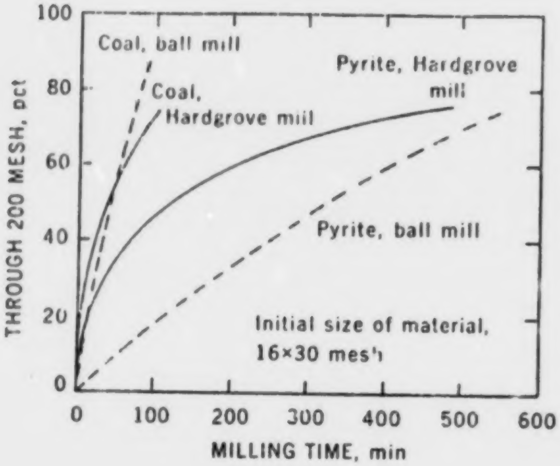


FIGURE 2. GRINDABILITY OF PITTSBURGH SEAM COAL AND PYRITIC MATERIAL BY BALL AND HARDGROVE MILLS(10,11)

pulverized for combustion in large boilers. The coal fraction was 85 to 90 percent through 200 mesh and suggested that air classification following the controlled grinding may effect a separation.(10,11)

Such observations have been supported by microscopic analysis of minus 14-mesh coal samples in which the mean pyrite particle size ranged from 20 to 400 microns.(12) The proportions of pyrite contained in the coal particle (to an extent of more than 50 percent by volume) ranged from 20 to 95 percent.

Glenn and Harris estimated the size of pyrite grains using "micrometric methods".(13) They found that 70 to 98 percent of the pyrite grains are smaller than 20 microns and only 0 to 2.4 percent are 75 to 250 microns in size. On a weight basis, the pyrite grains less than 20 microns represent only 2.5 percent or less of the total weight of pyrite present in coal. For the three coals tested they found that most of the pyrite is found in grains larger than 75 microns (200 mesh) in size. They estimated that between 88 and 91 percent by weight of the pyrite was present in particles 75 to 250 microns in diameter. They concluded that if the pulverization proc is not too severe, larger pyrite particles would remain intact and, therefore would be separable from the coal which is normally crushed to 80 percent min 200 mesh. While the larger pyrite and associated mineral matter tend to concentrate in the plus-60-mesh fraction (250 micron), the fine imbedded pyri concentrates in the minus 200 mesh (<75 micron) fraction.

In a study undertaken to evaluate conventional mineral-crushing equipment available in 1962, improvements in the release of pyrite sulfur have also been observed when crushing to a top size of 1-1/2 inches starting with a coal size of 4 by 1-1/2 inches.(14) The test established that the single-roll crusher, which was the type most predominantly used in the coal industry, was the poorest type with respect to pyritic sulfur liberation, an subsequent sulfur removal upon cleaning at a specific gravity of 1.60 (18 percent rejection). Jaw crushers, coal "pactors", gyratory crushers, or "cuber" crushers were more suited for this purpose of primary size reduction (28 to 34 percent pyritic sulfur rejection).

In a study to determine the fate of trace elements during coal treatment before combustion, Shultz et al.(15) observed that the manganese concentration increased after crushing from values that were observed in the uncrushed coal. They considered the source to be the jaws of the crusher, which were made of manganese steel.

Chemical comminution has been done on a laboratory scale using moist liquid ammonia(16,17). The study showed the effectiveness of immersion in liquid ammonia for fragmenting bituminous coal after drying (i.e., removal of ammonia) in a manner that would permit subsequent removal of pyritic sulfur and ash-forming minerals without grinding to fine sizes. During the treatment, the bulk of the coal was unaffected and only those naturally occurring intrusions filled with contaminant material were affected. The interlayer forces between the contaminant and coal phases were weakened or destroyed by the ammonia. During subsequent fragmentation of the coal, cleavage occurs along these weakened boundaries to liberate the noncoal constituents from the coal matrix with only a minimum formation of extraneous fine-sized coal.

There is little direct evidence to support the postulated mechanism for chemical comminution process developed by the Syracuse University Research Corporation. In part this is due to the lack of understanding of the forces which hold coal, including the noncoal substances, together. Although no definite proof exists, it is generally assumed that the large coal polymers formed from humic acid substances during coal formation are bound together by hydrogen bonding which if disrupted by a chemical comminution agent would weaken the boundary between the coal and noncoal components and allow the massive coal to fall apart. Therefore, it appears that the process involves the rapid migration of certain low molecular weight compounds such as NH_3 and methanol throughout the naturally occurring system of faults in coal.(17) The chemical disrupts the bonding forces acting across the surfaces which constitute these internal boundaries, and the coal undergoes forceless breakage or chemical comminution. Although the mechanism was not fully defined, the chemical agents for comminution seem to induce the breakage in a highly selective manner along those internal boundaries previously weakened by the infiltration of mineral constituents, i.e., pyrite and ash. No significant dissolution of the matrix of the coals studied had been found nor was there reported any apparent interaction between the noncoal constituents and the comminuting agent. What resulted from the act of comminution was fragmented coal, from which the entrained pyrite and ash had been liberated. Since no grinding or mechanical inputs are involved, the size distribution of comminuted coal was governed by the internal fault system in the coal, the comminuting agent, and time of exposure. The comminuting agent did not appear to affect the coal impurities, the size of the pyrite or other mineral constituents as does mechanical size reduction.

It has been claimed by the Ilok Powder Company that, through a process of thermal-shock treatment at between 700 and 1000 C, coal can be reduced from a top size of 4 microns to 0.3 micron and simultaneously stripped of all contaminants--ash as well as organic and inorganic sulfur. Such a process requires an initial reduction of coal to a 4-micron size. Ilok Powder Company claimed that the comminution energy required for reducing 97 percent of the coal to 4 microns is 24.58 kWh/ton. This is about 7 percent of the energy that would be expected on the basis of the present state of the art for size reduction. The Ilok concept was reviewed in a special study for the Electric Power Research Institute because of the many potential advantages of such a process.(18) Although the findings of the study failed to corroborate the claims, it was believed that the basic idea should stimulate further research and development in coal comminution and beneficiation.(18,19) One inherent problem of such a process is the ultimate separation of the clean coal from the refuse at such a small particle size.(13)

2.1.4 Separation Methods Using Specific Gravity Differences

The separation of the coal from the refuse liberated during mining, size reduction, and screening (usually as mineral constituents and pyritic sulfur) involves the use of one of the basic principles described earlier. The methods employing these principles are discussed in a way which emphasizes the removal of pyritic sulfur rather than the mineral constituents important in reducing the ash content of coal. Unless specific mention is made of the effect of the method on the trace elements, their separation is assumed to follow their distribution in raw coals discussed in Section 2.1 (i.e., these trace elements known to be associated with the organic part of coal would remain with the coal fraction, while trace elements more commonly associated with the mineral matter contained in raw coal would be removed with the noncoal fraction.)

This section deals with separation methods based on specific-gravity differences of coal and its impurities and the effectiveness of such methods for removing pyritic sulfur from coal. Table 3 summarizes the methods covered in this section.

Washing Methods. Washing processes in current use utilize different technologies and each process has varying amounts of art involved. These processes depend primarily on the influence that flowing water has on materials of different specific gravity, i.e., differences in the specific gravity of coal relative to noncoal entities in run-of-the-mine coal. The mechanisms by which transport and subsequent separation occur are complex functions of the particle (volume, specific gravity, shape, etc.), the fluid (velocity, viscosity, etc.), the device geometry, and system parameters.(3)

Jigs and launders are used to remove refuse from freshly mined coal that has been screened to a top size of 3 to 4 inches and a bottom size of 3/8 inch (in some cases 1/4 inch). Washing coal in these devices removes large-size refuse such as pyrites and shale and puts some clay into suspension. Specially designed jigs and launders can treat coals finer than 1/2 inch to remove finer-size refuse, including pyrites. These devices are again beginning to be used in the United States.(20,21) Performance data specific to sulfur reduction could only be inferred from the extent of coal-ash reduction.

Wet concentrating tables augment the separation effect of water flow with mechanical motion. Such devices are well suited for removing refuse from coal in the 3/8-inch to 35-mesh (0.42 mm) size range. The effectiveness of this method on sulfur reduction is shown in Table 4 under the column designated rough-cleaned coal.(22) Pyritic sulfur was reduced from 4.1 to 50.7 percent, depending on the coal being processed. The extent of removal did not appear to have much correlation with amount of pyritic sulfur present in the coal.(22) By crushing the cleaned coal to minus 30 mesh and cleaning it again, further reductions in pyritic sulfur and ash were obtained, as shown in Table 4 under the column designated deep-cleaned.

TABLE 3. GRAVITY SEPARATION METHODS

Method of Separation	Size of Typical Feed	Status of Use	Contaminants Removed and Performance	Reference
Washing				
Jigs, launders	4 to 1/4-inch	Commercial, 45 percent of tonnage[a]	Shale, clay, sand, large pyrite; about 15-30 percent of pyritic sulfur removed[b]	3
Feldspar jigs	minus 3/8-inch	Limited	Small pyrite, sand, shale	3
Concentrating Table	3/8-inch to 35-mesh	Commercial, 14 percent[a]	Shale, clay, small pyrite see Table in text for performance	
	minus 30-mesh	Experimental		
Hydroclone	minus 1/4-inch	Commercial	Fine pyrite; ~ 20% reduction in total sulfur	23
Concentrating Spiral (e.g., Hymphrey Spiral)	minus 30-mesh	Commercial and Experimental	Fine pyrite; ~ 15% reduction in total sulfur	23
Dense Medium				
Laminar Flow	4- to 1/4-inch	Commercial, 31 percent[a]	Clays, shale, sand, large pyrite	3
Cyclone	3/8-inch to 32-mesh	Commercial	Fine refuse and pyrite	3
Air Concentration				
Jigs, tables, launders	3/8-inch to 48-mesh	Use diminishing	Pyrite, clay, sand	3
Classifiers	80% minus 200-mesh (p.c. grind)	Commercial, Experimental	Fine pyrite; reduction 30-60%	23
Centrifugal	70% minus 200-mesh	Experimental	Fine pyrite; reduction 60%	11

(a) Source reference (21).

(b) The amount removed depends on type of crusher used and nature pyrite in raw coal.

TABLE 4. REDUCTION OF ASH AND PYRITIC SULFUR FROM DIRECT TWO-STAGE CONCENTRATION TABLE CLEANING(22)

Sample of Coal Seam	ROM Coal, Weight Percent			Rough Cleaned, 3/8" x 0, percent reduction		Deep Cleaned, 30 mesh x 0, percent reduction		Overall Reduction, percent		Coal Recovery, percent
	Ash	Org S	Pyrit S	Ash	Pyrit S	Ash	Pyrit S	Ash	Pyrit S	
W. Ky. No. 6 Butler Co., Ky.	10.0	0.80	4.66	36.6	29.0	23.4	2.6	51.5	30.8	94.2
Bakerstown Seam Grant Co., W. Va.	24.0	0.46	2.42	35.0	50.7	19.9	22.5	47.9	61.8	78.4
Lower Kittanning Westmoreland Co., Pa.	26.4	0.52	3.64	58.7	41.6	30.3	22.1	71.2	54.5	68.2
Lower Freeport Indiana Co., Pa.	19.9	0.42	1.42	29.6	22.6	27.9	15.3	49.2	34.4	79.4
Ft. Scott Rogers Co., Okla.	13.3	1.17	2.96	38.3	11.2	34.1	4.0	59.4	14.7	88.7
Lower Freeport Butler Co.	15.0	0.54	2.78	6.7	15.8	15.0	24.7	20.7	36.6	91.2
Baxter Crawford Co., Kan.	14.8	0.78	3.23	16.2	10.0	17.2	13.0	31.1	21.6	94.5
Clements Walker Co., Ala.	25.3	0.54	1.42	55.7	4.1	35.7	8.0	71.5	11.7	78.7
Average Reduction (for the 8 coals)				34.6	23.1	25.5	14.0	50.3	33.3	84.2

The overall sulfur reduction obtained by staged table concentration was consistent with that expected from a laboratory float-sink evaluation at a specific gravity of 1.6.

The hydroclone (which is differentiated from cyclones used in dense-media separation discussed later) uses water instead of an artificial gravity suspension medium with a specific gravity greater than 1. However, it is believed to utilize an autogenous dense-medium developed from the raw coal being cleaned.(3,23) It is used to clean flotation-size coal (minus 28 mesh) if the coal is not amenable to flotation. However, it is not applicable for difficult-to-clean coals or separations at a low specific gravity. The hydroclone has been reported superior to flotation for lowering the sulfur content of some washed coal, if fine pyrite is present in the feed.(3) Bituminous Coal Research, Inc., evaluated a hydroclone with a 30 mesh by zero raw coal containing about 2.43 percent total sulfur. The total sulfur reduction in two experiments was 21 and 28 percent with a coal recovery of 91 percent in each case.

The Bureau of Mines evaluated hydroclone coal washers in actual plant operations to determine sharpness and efficiency of separation that might be anticipated in commercial operation.(24) In overall performance, coals with top sizes of 1/4 inch and 8 mesh were deemed satisfactory in that good clean coal was produced. However, the rejects contained "misplaced coal in amounts sufficient to require secondary recovery. Another drawback is the large water flow required for proper operation. Despite these drawbacks, hydroclones have gained acceptance in the United States because of the large tonnage they can process at modest capital investment and their ability to remove fine-size pyrite. Typical results on pyrite removal at four commercial installations are given in Table 5.

Spiral concentrators were evaluated on an experimental basis and were able to remove ~ 15 percent of the total sulfur from a minus 30 mesh coal containing 2.90 percent sulfur. In this study, its use as a second stage in a two-stage process was more effective than the concentrating table alone.(23)

Dense-Media Separation. The theoretical and practical aspects of various dense medium processes have been discussed extensively in the

TABLE 5. PYRITIC SULFUR REMOVAL BY HYDROCLONES IN COMMERCIAL USE(24)

	Plant A	Plant B	Plant C	Plant D-2
Coal Feed Size	Minus 8-mesh	Minus 4-mesh	Minus 1/4-inch	Minus 8-mesh
Pyritic Sulfur, percent	0.24	0.42	2.38	2.40
Clean Coal Size	8 x 200 mesh	4 x 200 mesh	1/4-inch x 325 mesh	8 x 325 mesh
Pyritic Sulfur, percent	0.13	0.25	1.29	0.64
Recovery Efficiency, percent (a)	93	86.8	70.6	72.8

(a) Recovery efficiency was based on the amount of coal recovered versus that recoverable in washability tests at a specific gravity of 1.87.

literature(1-4) and for this reason are not described in any greater detail here than what is presented in the following paragraphs. The dense medium processes use various approaches to attain specific gravities greater than 1. The application of the dense-medium separation process is a practical extension of the laboratory float-sink test. Such processes do not exactly duplicate the laboratory float-sink separations for the following reasons.(3)

- Suspensions rather than liquids are usually employed as separating media.
- The introduction of feed and removal of float-and-sink components introduce disturbances in the medium.
- Agitations and currents in the vessels are required to keep the separating medium in suspension.
- Retention time for perfect separation is usually insufficient for separating near-gravity material.

Although any practical-size particle could theoretically be treated by dense-medium processes, the practical lower size limit for laminar-flow dense-medium separators is 1/4 inch (6.4 mm). Coals in the size range 0.5 to 6.4 mm are normally processed in separators employing centrifugal force, e.g., dense-medium cyclone washer.

Four types of separating media have been or are being used:(3)

(1) Organic liquids in the specific-gravity range 0.89 to 2.96. They have not been used commercially although a 50-tph pilot plant was built by the E. I. du Pont Company for treating anthracite. Typically halogenated hydrocarbons such as tetrabromoethane (sp gr 2.96), pentachloroethane (sp gr 1.68), and trichloroethane (sp gr 1.46) or mixtures of them are used. Loss of the medium through adsorption by the coal or refuse is minimized by treatment with water soluble active agents. Equipment using halogenated organic liquids must be vapor sealed to prevent loss and limit toxic effects of the vapors.

(2) Water solutions of calcium chloride or zinc chloride have been used. The actual densities of 1.14 to 1.25 are increased by controlled circulation.(3)

(3) Use of suspensions of solids in water is the prominant medium being used in the United States. The stability of suspensions used in coal separation processes ranges from that of nearly stable suspensions of ultrafine magnetite (-325 mesh) to that of less-stable baryte suspensions to that of unstable suspensions of coarse sand.

(4) A bed of sand fluidized with air acts as a heavy fluid, and separators using the principle have been designed and tried.

Laminar-flow dense-medium separators employed on coal coarser than 1/4 inch (6.4 mm) are efficient, and coal recovery is between 95 and 99 percent of the values expected from laboratory float-sink tests.(3) Excellent descriptions of such pieces of equipment are given in reviews.(1,3) Pyritic sulfur removal in such systems will fall short of the potential determined from laboratory float-sink evaluations. The performances of commercial dense-medium operations have been evaluated with respect to ash removal, but no data on which pyritic sulfur removal could be evaluated were given.(25)

Dense-medium separators employing centrifugal forces are used to remove refuse (and pyritic contaminants) from fine coal with the size range 0.5 mm to 14 mesh (6.4 mm). These devices are called dense-medium cyclones.(3) In a typical device, a mixture of medium and raw coal enters tangentially near the top (as shown in Figure 3) of the cylindrical section, thus forming a vortical flow. The refuse moves along the wall of the cyclone and is discharged through the underflow orifice. The washed coal moves toward the longitudinal axis of the cyclone and passes through the vortex finder to the overflow chamber. In a typical cyclone, the centrifugal force acting

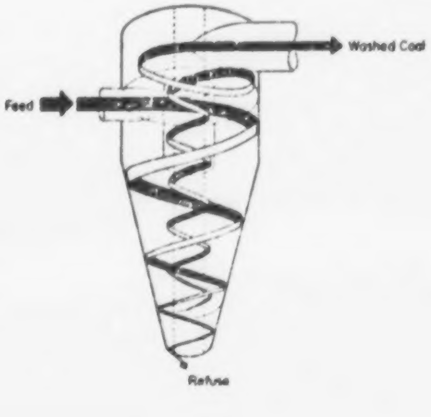


FIGURE 3. IDEALIZED FLOW PATTERN OF DENSE MEDIUM CYCLONE(3)

on a particle in the inlet region is about 20 times greater than the gravitational force in a static bath.(3) In performance, the dense-medium cyclone effects sharper separation between coal and impurity than can be obtained in other types of cleaners handling the same size range. Because such devices can handle smaller size coal, one would expect a greater degree of pyritic sulfur removal, typical of a smaller size coal fraction (see Figure 1 and Table 4). In a study of dense-medium cycloning of coals with sizes down to 100 mesh (0.149 mm) using a solution of zinc chloride and magnetite suspension, Deurbrouck concluded that the finer coal size improves the separation.(26) No values other than those for ash removal were given. The inherent problem of using such a fine-size coal feed in a large-scale operation employing a suspension of magnetite as the dense medium is the recovery of the fine magnetite.

Air Classification Methods. The principles of air classification have been used by the mineral-processing industries for several years. The use of air classifiers as a means of removing pyrite from the coal fed to the burners at power stations has been investigated on a laboratory scale.(10,11) Such a process separates a relatively coarse grind of pulverized coal into a fine fraction suitable for firing a p.c. grind (70 percent minus 200 mesh) and a coarse pyrite-rich fraction that requires further processing. Typicall the pyritic sulfur is reduced from 30 to 60 percent for the ten samples studied. Coal recovery for a single pass ranged from 78 to 94 percent. Jigs, tables, and launders using air as a separating medium have been used for coal in size range 3/8 inch to 48 mesh. However, their use has declined because of problems with processing wet coal (from the mine face) and the associated dust. Despite these shortcomings, investigations into the processing of p.c.-grind coals for pyrite removal by other devices continue. For example, centrifugal separators, which are used to dedust large aggregate or separate ground materials into small- and large-particle-size fractions, have been evaluated for coal on a laboratory scale.(10,11) Maximum rejection of pyrite (60 percent) was obtained when the initial size of the feed was minus 270 to plus 400 mesh (0.063 to 0.037 mm). The capability of centrifugal separation to remove pyritic sulfur from various size fractions obtained from p.c. ground coal (i.e., 70 percent minus 200 mesh) is shown in Figure 4.(11)

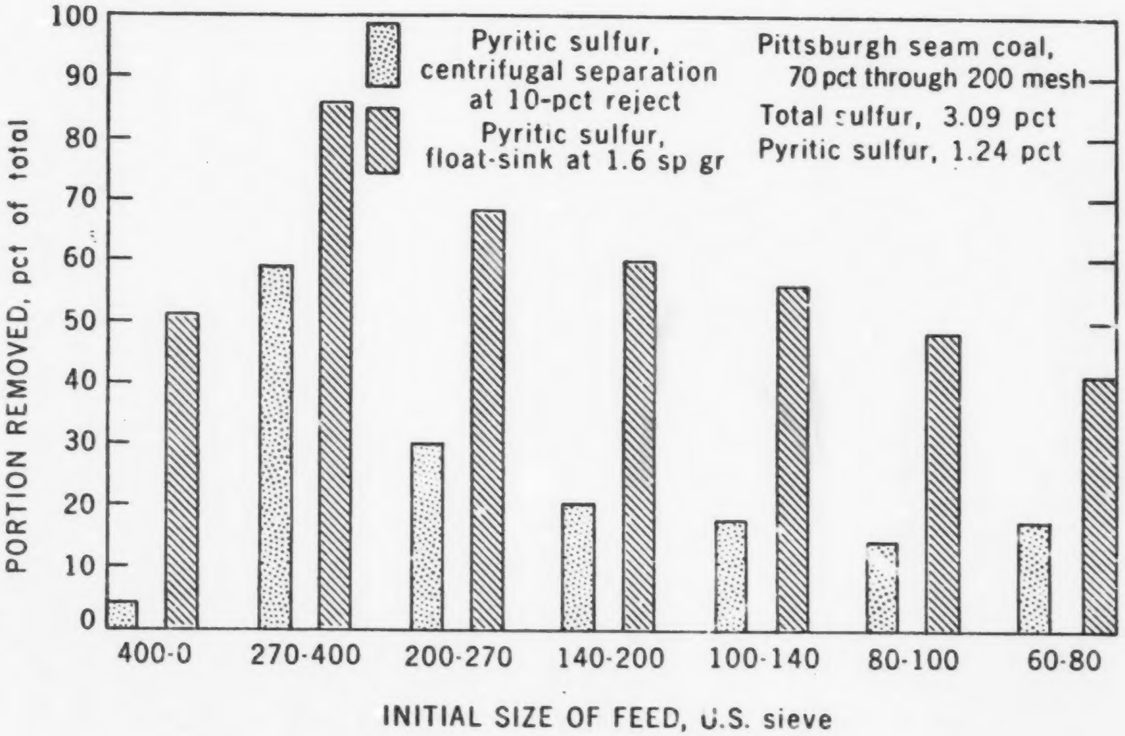


FIGURE 4. REMOVAL OF PYRITE FROM CLOSELY SIZED FRACTIONS OF FINELY GROUND PITTSBURGH SEAM COAL BY CENTRIFUGAL SEPARATION(11)

2.1.5 Separation Methods Based on Surface-Property Differences

This section discusses the methods of removal of pyritic sulfur and ash mineral from coal based on differences in such surface properties as wettability, surface charge retention, and colloidal properties. The methods summarized in Table 6 are described in greater detail below with respect to the coal size studied and the performance of the method especially as it relates to pyrite removal.

Froth Flotation Methods. The flotation process depends on the selective adhesion to air of some solids and the simultaneous adhesion to water of other solids. A separation of coal from coal wastes then occurs as finely disseminated air bubbles are passed through a feed coal slurry. Particles adhering to the air bubbles (usually coal) are separated from nonadhering particles as the bubbles float to the surface of the slurry and are then removed as a concentrate. Because of the variability in coal composition and floatability, careful selection of frothing agents, surface-modifying agents, and chemical collectors to suit coal types is essential. Because the surface properties of coal and fresh pyrite do not differ greatly, the fine particle size pyrite tends to float with the clean coal unless pyrite depressants are employed.(3) Precisely controlled concentrations of ferrous sulfate and hydrolyzed metal ions have been found effective as pyrite depressants.(27,28) The use of known depressant reagents for pyrite in the mineral dressing industry such as zinc sulfate potassium permanganete, potassium dichromate, lime and sodium cyanide, has met with no great sucess.(29) No truly selective reagents acting as pyrite depressants were found during the study.(29) The major factors affecting coal flotation are:

- Particle size of feed coal
- Oxidation and rank of coal
- Pulp density of slurry
- pH of water and other water characteristics
- Flotation reagents
- Flotation equipment.

TABLE 6. SEPARATION METHODS BASED ON SURFACE PROPERTY DIFFERENCES

Method of Separation	Typical Feed Size	Status of Use	Contaminants Removed and Performance	Reference Number
Froth Flotation		Commercial	Fine pyrite and ash minerals	
Conventional	minus 28 mesh	4 percent[(a)]	~ 50 percent pyrite removal	26
Two-Stage	minus 28 mesh	Pilot Plant	50-80 percent pyrite removal	27-34
Vacuum	minus 14 mesh	Experiment	Evaluated on ash removal, less than mechanical flotation method.	35
Immisibible Fluid				
Trent	minus 28 mesh to	Experimental	Ash removal some pyrite	36-38
Convertol	minus 325 mesh	Pilot	Ash removal some pyrite	
Spherical Agglomeration Variations		Experimental	Ash, 50-90 percent pyrite removed and trace elements	39-44
Electrophoretic	minus 200 mesh	Experimental	Pyritic sulfur and ash (Considered Impractical)	54-55
Selective Flocculation	40 micron or less	Commercial	Removal of coal from suspended ash minerals or visa versa	47-48
Electrostatic	75 percent minus 200 mesh	Experimental Pilot	Removal of 30-50 percent of pyrite	62

(a) Reference (178).

The optimum size range of coal for feed to flotation circuits is between 48 and 150 mesh. However, the size range is dependent on the pulp density being employed. Current practice in the United States varies from 3 to 20 percent with an approximate average of 7 percent. In general, the coarser the feed, the higher the pulp density; and the finer the coal, the lower the pulp density. When a pulp density of 4 to 5 percent is used, the particle size of the feed can be as fine as 80 to 90 percent minus 325 mesh.(Since consistent surface properties are essential for uniform froth-flotation operation, oxidation of the coal (weathering) should be held to a minimum or compensated for. Variations in surface properties due to coal rank can be adjusted to suit the coal being processed. Generally, low-volatile coals are easier to float than most high-volatile coals, and lignite is the least floatable.(3,30) The pH of the slurry affects both recovery and the quality of the product. The optimum pH varies with the coal type.

The performance of flotation operations has been based on float-sink analyses. These analyses usually indicate that a better product should be obtained than froth flotation provides.(30) In most instances, only a small part of the 1.8-specific-gravity sink material was recovered by flotation. Conversely, the ash content of the flotation tailings was usually higher, indicating that froth flotation is selective even when only high ash impurities are involved. A partial explanation for this is the finely disseminated nature of pyrite in coal. Frequently, the pyrite is encased in coal and floats. In addition, unless the pyrite depressant reagent is effective, the very fine material will float with the coal. In both laboratory and commercial coal froth-flotation operations, between 40 to 60 percent of the pyrite remains in the cleaned coal.(29,31) However, the fine ash content is reduced significantly. Typical results for froth flotation of British coals of different sulfur contents are given in Table 7, and a summary of a plant performance evaluation is given in Table 8.

This inability to remove about one-half of the pyrite is inherent to many of the United States coals as well. In several early EPA-sponsored laboratory studies conducted at the U.S. Bureau of Mines, it was found that even though much of the pyrite in fine-sized coal could be rejected with the high-ash refuse, a portion of the pyrite could not be removed under optimum

TABLE 7. TYPICAL RESULTS OF FROTH FLOTATION OF BRITISH COALS OF DIFFERENT SULFUR CONTENT(29)

Raw Coal, percent sulfur		Clean Coal, percent sulfur	
Total	Pyritic	Total	Pyritic
1.6	0.8	1.4	0.4
2.4	1.6	1.8	0.8
3.2	2.4	2.2	1.2
4.0	3.2	2.6	1.6
4.8	4.0	3.0	2.0

TABLE 8. SUMMARY OF FROTH FLOTATION PLANT PERFORMANCE TEST(31)

Feed, percent		Float, percent		Tailings, percent	
Ash	Pyritic Sulfur	Ash	Pyritic Sulfur	Ash	Pyritic Sulfur
32.7	2.01	7.5	1.16	68	5.45

conditions for froth flotation of the coal. This was attributed to too fine a coal size so that pyrite became entrapped in the froth or became attached to floatable coal.(32) Research and development aimed at improving or modifying the froth-flotation process for better pyritic sulfur rejection resulted in a two-stage flotation process in which a second-stage flotation was used. In the second stage, pyrite was floated away from the coal cleaned in the first stage using xanthate as a pyrite floater while the coal was depressed with hydrophylic colloid. In the laboratory study, the pyritic sulfur of a minus 35-mesh coal from the Lower Freeport bed was reduced from 1.78 percent to a range of 0.75 to 1.06 percent in the first stage and then to 0.27 to 0.82 percent in the second stage. In the pilot-plant evaluation, similar results were obtained.(32-34) The results of both studies are given in Table 9.

In the first stage, the frother used was methylisobutylcarbinol (MIBC) and the optimum pH was between 8.0 and 8.5. In the second stage a commercial coal depressant was used and hydrochloric acid was added to adjust the pH to about 6 to 6.5 followed by the addition of potassium amyl xanthate (pyrite collector) and MIBC. Overall, the coal recoveries were 62 to 65 percent which represented 80 to 85 percent of the combustible material in the raw coal.(34) The coal recovery in the second stage was between 90 and 95 percent. About 30 percent of the pyrite remained in the difficult-to-clean Pittsburgh coal and about 40 percent remained in the Lower Freeport coal.

Vacuum flotation is a concept of using reduced pressures over slurries to effect froth formation. Such a system was evaluated against mechanical froth flotation and was found to be much less efficient in ash removal than were the mechanical cells.(35) However, several advantages were noted. One was that no froth handling existed because when the vacuum was released, the froth broke down completely. Another advantage was that the number of moving parts immersed in the pulp was at a minimum and that this process required only 25 percent of the power per ton per hour of sludge required for mechanical flotation. Problems inherent with a large-scale vacuum system and the need for long barometric legs were given as disadvantages.(35)

TABLE 9. RESULTS FROM TWO-STAGE FROTH FLOTATION REMOVAL OF PYRITE SULFUR[32-34]

Feed Coal Minus 35 Mesh	Sulfur, Percent						Ash, Percent			Coal Recovery, Percent	
	Feed		First Stage		Second Stage						
	Pyritic	Total	Pyritic	Total	Pyritic	Total	Feed	First Stage	Second Stage	Overall	Second Stage
Pittsburgh Bed											
Laboratory	1.27	1.70	0.89	1.57	0.43	1.14	30.8	9.2	8.2	60.6	92-95
Pilot Plant	1.05	1.51	0.90	1.59	0.52	1.20	31.6	10.1	9.7	56-62	
Lower Freeport Bed											
Laboratory	2.32	2.65	0.80	1.29	0.28	0.97	30.5	7.3	6.8	52.6	90-95
	2.32	2.65	0.77	1.32	0.37	0.99	30.5	7.2	6.7	57.5	
Pilot Plant	2.19	2.57	0.87	1.40	0.55	1.12	31.8	7.8	7.5	56-60	

Immiscible Liquid Agglomeration Methods. The use of water-immiscible liquids, usually hydrocarbons, to separate coal from its impurities is an extension of the principles employed in froth flotation. The hydrocarbons wet the hydrophobic surface of coal (either directly if the hydrocarbons are used on dry coal, or by displacement of water from the surface when an aqueous slurry is treated) and the mineral impurities which are hydrophylic are brought into or remain in aqueous suspension. Separation of the two phases takes place after agglomeration or coalescence occurs and produces a clean coal containing some oil and an aqueous suspension of the refuse generally free of combustible material. The particle size of the raw coal used in a process based on these principles must be minus 28 mesh (0.149 mm) or less for effective separation. For this reason, the principle can be used for the recovery of coal values from minus 200-mesh slimes obtained from various coal-washing operations.

Over the period 1920 through 1975, three processes based on this principle have been reported in the literature. They are the Trent process, the Convertol process, and the spherical agglomeration process. The Trent process was the earliest and was developed to remove ash from powdered coal during World War 1.(1,36) The U.S. Bureau of Mines investigated the underlying physical and chemical facts of the process in a laboratory study and published the findings.(37,38) In the process, powdered coal, water, and oil were agitated together in such a way as to produce a partly deashed plastic fuel called an amalgam. The oil selected the coal particles and largely excluded the water and ash. The amalgam was freed of water by mechanical kneading. The potential impact of the process was that wet grinding became attractive, lower grade coals could be used, and the product was suitable feed for coking and gasification processes. In addition, the concept could be used to break and dehydrate coal-tar emulsions with powdered coal.

The Bureau of Mines study determined the varieties of coals that could be treated and the ash and sulfur removal that could be attained by the Trent process. The performance of the Trent process on coals ground to pass through a 65-mesh screen is shown in Table 10. As anticipated, the materials readily wet by water were easily removed, i.e., shale, clay, and gypsum, while materials showing preference for wetting with oil were removed

TABLE 10. SUMMARY OF TRENT PROCESS EVALUATION(37)

Kind of Coal	Raw Coal, percent			Cleaned Coal, percent			Efficiency, percent		
		Sulfur			Sulfur		Reduction		Combustible
	Ash	Total	Pyritic	Ash	Total	Pyritic	Ash	Total Sulfur	Recovery
Anthracite I	27.7	1.00	-	7.0	0.70	-	74.7	30	97.8
Anthracite II	31.5	1.74	1.21	7.0	0.85	0.13	79.2	48	98.0
Bituminous, bone coal refuse	21.7	0.93	-	12.5	0.80	-	42.3	14	99.4
Bituminous, Illinois	16.6	5.33	-	7.4	5.28	-	55.4	1	89.8
Bituminous, Indiana	9.9	4.38	-	6.3	4.27	-	36.4	3	99.8
Bituminous, Oklahoma	19.5	4.74	3.01	5.7	3.75	2.10	70.8	35	83.5
Bituminous Refuse, Tennessee	63.5	1.64	-	20.6	1.48	-	67.7	10	77.8
Bituminous, Brazil	35.6	2.47	-	9.4	2.32	-	73.6	6	97.0
Lignite, California(a)	35.1	1.77	-	25.7	1.56	-	26.8	12	95.0
Lignite, Texas(a)	33.5	1.44	-	18.1	1.42	-	46.0	1	100.0

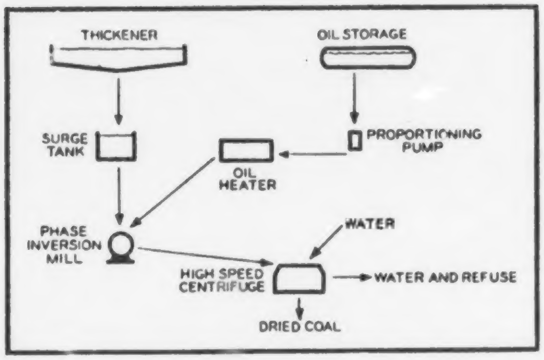
(a) Carbonized at 500 C.

with difficulty, i.e., pyrite, especially in the fine state formed during pulverization. Differences were noted in the behavior of pyrite in anthracite and bituminous coals. Size reduction to -200 mesh appeared to yield maximum removal, while reduction to -600 mesh or finer gave no separation of pyrite. When coal pyrite was used alone, an amalgam could be made of it alone, and very little remained in aqueous suspension. Such behavior suggested that the preliminary washing for pyrite removal should be done before the Trent process is used. The potential for ash removal of 30 to 75 percent, as shown in Table 10, continues to be attractive, especially since the amalgam could be so readily dewatered (5 percent after kneading). The process was not considered suitable for processing lignites unless the lignite had been charred at 500 C.

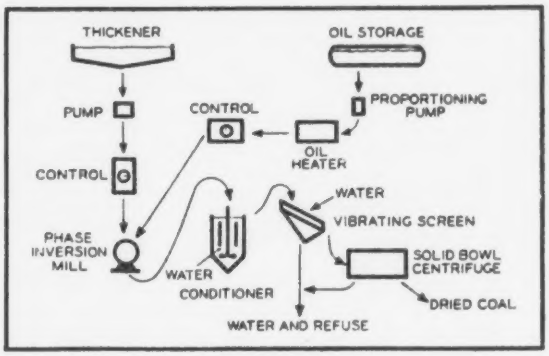
The Convertol process, which was developed in Germany, was investigated on a pilot scale by the U.S. Steel Corporation for the purpose of recovery of acceptable coal from washery slimes, i.e., minus 200-mesh coal equivalent to 2.0 to 2.5 percent of raw-coal input.(39) A second unit was also installed which incorporated modifications of the German process. The same principles used in the Trent process apply to the Convertol process as well.

Modifications (incorporated by the U.S. Steel Corporation) needed to better dewater the oiled coal agglomerate included the addition of a vibrating screen and a solid bowl centrifuge as shown in Figure 5. This arrangement handled a feed of over 80 percent minus 200-mesh material analyzing 24 percent ash and 0.7 percent sulfur (dry basis). The material recovered contained approximately 11 percent ash, 0.7 percent sulfur, and 25 percent moisture.

Further evaluation of the performance of the Convertol process with respect to various operating parameters was reported by Sun and McMorriss.(40) They demonstrated that the three coals they studied differ appreciably from each other not only in surface components but also in size distribution, and consequently had different affinities for any given agglomeration reagent. Removal of sulfur was again shown to be poor and one of the better results using kerosene reduced the sulfur from 1.80 to 1.62 percent, while the ash was reduced from 15.85 to about 5.0 percent.


THICKENER
OIL STORAGE
SURGE TANK
PROPORTIONING PUMP
OIL HEATER
PHASE INVERSION MILL
WATER
HIGH SPEED CENTRIFUGE
WATER AND REFUSE
DRIED COAL

(a) Typical German Convertol Plant


THICKENER
OIL STORAGE
PUMP
CONTROL
PROPORTIONING PUMP
OIL HEATER
CONTROL
WATER
VIBRATING SCREEN
PHASE INVERSION MILL
WATER CONDITIONER
SOLID BOWL CENTRIFUGE
DRIED COAL
WATER AND REFUSE

(b) U.S. Steel Corporation Modified Convertol Plant

FIGURE 5. SEQUENCES IN GERMAN AND UNITED STATES CONVERTOL PROCESSES(39)

The extension of successful spherical-oil agglomeration techniques used in mineral processing to fine-coal beneficiation has been reported recently.(41-46) In particular, improvement of the extent of pyrite removal has been the subject of laboratory batch experiments.(44) In order to reduce the hydrophobic character of pyrite, which was compounded by its 1 to 2-micron size, several known pyrite depressants were tried at neutral, basic and acidic pH ranges. The coal was ground to 100 percent less than 50 microns and 70 percent less than 20 microns. The best results were those given in Table 11. About 50 percent of the pyritic sulfur was removed.(44) The surface of the pyrite could also be altered during grinding by mixing waste coal known to contain bacteria of the Ferrobacillus-Thiobacillus group Analysis of the agglomerated product from such a treatment showed that more than 90 percent of the pyritic sulfur had been removed. It was postulated that the surface of the pyrite was oxidized by the same bacteria action that causes the pyrite to be converted to sulfate. The treatment conditions and the agglomerate analysis are given in Table 12.

Capes et al.(45) investigated the effect of fine grinding of coal followed by oil agglomeration of the carbonaceous constituent on the rejection of trace quantities of heavy metals. Six coals, mainly from the U.S. and Canada, were treated. Many of the trace metals were subsequently reduced during this type of beneficiation process. Those metals associated with the organic material in coal remained with the agglomerated product.

In the process, the coal was ground as a 40 to 50 weight percent aqueous slurry to a consist of 100 percent minus 200-mesh and 40 to 50 perce minus 325-mesh particles. Feed material for power stations which had been dry pulverized to approximately 100 percent minus 60 mesh and 30 percent minus 325 mesh were also evaluated at 10 percent slurries. A light petrole distillate was added to the slurry at a loading of 10 to 30 percent of the dry-solids weight and agitated in a blender for 5 minutes. The mixture was "filtered" through a 100-mesh screen to allow the water containing the tailings to drain away. The trace-element analysis of the tailings and th beneficiated coals is given in Table 13. In every use better than 90 percer

TABLE 11. EFFECT OF DEPRESSANTS ON PYRITE REMOVAL DURING AGGLOMERATION (NEW BRUNSWICK, CANADA, COAL)(44)

Depressant Used	Run of Mine Coal, %[a]					Clean Coal, %[a]	
	Ash	Sulfur				Ash	Total Sulfur
		Total	Sulfate	Pyritic	Organic		
None	16-20	6.6-8.0	0.1-0.3	6.0-6.4	1.4-1.7	6.8	5.9
NaCN	16-20	6.6-8.0	0.1-0.3	6.0-6.4	1.4-1.7	5.8	4.4
Na_2CO_3	16-20	6.6-8.0	0.1-0.3	6.0-6.4	1.4-1.7	5.5	4 to 5
$K_4Fe(CN)_6$	16-20	6.6-8.0	0.1-0.3	6.0-6.4	1.4-1.7	5.8 to 7.3	4 to 5
$K_3Fe(CN)_6$	16-20	6.6-8.0	0.1-0.3	6.0-6.4	1.4-1.7	4.8 to 5.7	4 to 4.5

(a) Dry basis.

TABLE 12. EFFECT OF THE PRESENCE OF THE BACTERIA FERROBACILLUS-FERROOXIDONS DURING GRINDING ON PYRITE REMOVAL DURING AGGLOMERATION (NEW BRUNSWICK, CANADA, COAL(a)(44))

Treatment	pH During Agglomeration	Agglomerate, percent	
		Ash	Sulfur
Ground with 20% waste New Brunswick Coal	6.8 to 7.0	7.0	2.7
Ground with 40% waste New Brunswick Coal	5.9 to 7.3	5.5	2.5
Ground with bacteria grown from waste New Brunswick coal. Equivalent to 10% waste coal.	7.3 to 8.0	4.1	2.3

(a) Raw-coal analysis same as in Table 11.

TABLE 13. SUMMARY OF RESULTS ON TRACE-ELEMENT REMOVAL BY OIL AGGLOMERATION(45)

Element	Average Concentrations, ppm[(a)] Feed Coal	Agglomerates	Tailings	Ratio of % element rejected/ % ash rejected, avg
Aluminum	15,000	10,000	100,000	0.88
Antimony	1.3	0.7	7	0.68
Arsenic	72	15	270	1.11
Barium	40	38	100	0.42
Beryllium	0.5	0.7	0.03	0.02
Boron	21	18.8	32	0.49
Cadmium	0.3	0	2.0	1.23
Calcium	2,200	1,300	4,800	0.65
Chromium	652	186	2,837	0.90
Copper	301	171	1,103	0.79
Germanium	14	14	0	0
Iron	49,000	15,700	193,500	0.89
Lead	75	33	242	0.90
Magnesium	250	125	1,500	0.88
Manganese	275	55	935	0.97
Mercury	0.49	0.41	1.2	0.51
Molybdenum	183	43	667	1.01
Nickel	59	24	204	0.88
Selenium	4	3	20	0.44
Sodium	50	25	500	1.48
Tin	65	20	170	0.90
Titanium	425	400	710	0.33
Vanadium	150	61	410	0.87
Zinc	284	144	1,150	0.84
Zirconium	25	25	100	0.42

(a) All analyses are on a moisture-free basis.

of the combustible content of the feed was recovered. An examination of the ratio of element rejection to overall ash rejection suggests that many trace elements are concentrated in the tailings from this process. Those elements with ratios less than 0.5 were considered to be part of the organic constituents and were separated with the agglomerated product. Of these, the most obvious were Ba, Be, B, Ge, Hg, Se, Ti, and Zr. This trend is similar to the trends discussed for the distribution of trace elements in coal characterized in the first volume of this report.

Selective Flocculation Methods. Selective flocculation involves the aggregation of mineral grains into flocs without affecting the dispersion of other solids in suspension. The flocs are subsequently separated from the remaining solids by gravity methods. The literature on selective flocculation of coal slurries containing particles of 40 microns or less describes several specific surfactants that are found effective for flocculation of either the clean coal or coal impurities. Table 14 provides a partial list of selective flocculation reagents reported in recent literature. These are in addition to those reported and investigated in earlier works.(47, Although separation of coal from ash minerals such as shale and clays has been documented, no specific data on pyritic sulfur and trace-element reduction were given.

Electrophoretic-Specific Gravity Separation of Pyrite from Coal. In a laboratory-scale experiment, electrophoresis was employed in an attempt to overcome the problems associated with fine particles encountered in mining and coal preparation.(54) Electrophoresis is defined as the migration of electrokinetically charged particles in aqueous suspension toward an electrode of opposite charge in a direct-current electric field. The migration speed is directly proportional to the applied voltage and to the magnitude of the electrokinetic charge or zeta potential of the particles, and inversely proportional to the distance between the electrodes. It has found extensive use on colloidal systems, but not on material with coarser particles such as the coals below 100 mesh.

TABLE 14. SURFACE ACTIVE SUBSTANCES USED IN SELECTIVE FLOCCULATION OF COAL SLURRIES

Flocculant	Flocculant Dosage	Remarks	References
$C_{17}H_{35}COONa$	0.1-1 percent	Recommended as a specific flocculent for coal slurries (≪1 micron) in the presence of clay minerals. Sedimentation times of 25 to 50 hours are recommended.	49
Carboxy methyl cellulose in alkaline systems	>3-5 grams/cubic meter of solution at pH ~ 10	An effective coal flocculent for particle sizes below 40 microns; coal sedimentation rates of 8-10 mm/minute are reported.	50
Sodium polymethacrylate	5 grams/cubic meter of solution	A selective flocculent for coal slurries, predispersed with sodium silicate. Settling rates reportedly vary from 5 to 8 minutes/meter.	51
Soda ash and either sodium pyrophosphate or hexametaphosphate	pH values of 9-10 are recommended	Reportedly effective to flocculate anthracite fines from clay/coal suspension.	52
Polyacrylamide and sodium salts of sulfonated polystyrene	5-15.5 grams/m^3 of sulfonated polystyrene at pH 9.5	Recommended to maintain stable clay suspensions during coal coagulation and sedimentation.	52,53

With a high pyritic sulfur coal, migration of coal toward the negative electrode (anode) provided a separation of pyrite from coal at 200 to 500 volts. Because of the similarity between zeta potentials of coal and pyrite, separation was not effective without the supplementary use of the specific gravity differential between the two materials. Variations in the supporting electrolyte were not tried; however, even when distilled water was employed, the bubbles caused by the electrolysis of the water were found to be counterproductive. Use of domestic tap water also reduced the separations possible in distilled water.

In the study, both synthetic mixtures of pyrite and coal and high-pyrite coal crushed to minus 100 plus 325 mesh were used. The separation obtained with the synthetic mixture could not be realized with the high-pyri coal. In a further evaluation of the concept(55) it was concluded that the potential of electrophoretic separation had severe limitation for large-scale coal preparation and was considered uneconomical and impractical for commercial coal preparation. For example, because of the inherent characteristics of electrophoretic cells, the more promising arrangement would have been a battery of small cells. In such a case, a battery of cells large enough to clean one ton of coal per hour would require about 30,000 units the size of the laboratory device.

Electrostatic Separations. Much work has been done in the past 100 years with various types of electrostatic separators used for removing undesirable fractions from minerals, ores, seed, and a variety of other products. Electrostatic separation processes have been reported or proposed that make use of seven different basic phenomena: (1) "convection" or ion charging, (2) conductance and induction, (3) triboelectrification, (4) dielectric polarization, (5) dielectric hysteresis, (6) pyroelectric polarization, and (7) photoelectrification. Refinements to increase sensitivity have been tried, such as acid treatments, drying, heating, dusting with additives, dedusting, and exposure to ultraviolet radiation. Success has been reported under laboratory conditions and some processes have been used commercially. By far the most work on the separation of impurities from coal has been done using drum-type separators or chute-type separators. These separators were used on relatively coarse particles, generally larger than 150 mesh (0.1 mm).(56)

In an early U.S. patent by Schniewind, cited in Reference (56), an accurate account of the requirements for coal beneficiation was presented. Pyrite, which responded as a conductor, was the most easily removed impurity. For the remaining constituents of coal including slate, mineral charcoal, and coals of various rank, Schniewind specified controlling the humidity in order to obtain the selectivity required for electrostatic separation. Moisture control was considered to be essential for separations performed on softer coals. In Schniewind's process, the coal was dried, pyrite was removed from the dry coal by the electrostatic method, and then the coal was moistened for the removal of the shale. The hazard of a coal dust was reduced by adding flue gas (CO_2) to the separator chamber.

Up to the writing of the review by Fraas (1962)(56), no commercial applications of the electrostatic method of coal beneficiation had been reported. However, considerable work had been done in Germany beginning in about 1932. A review by Crawford of the German coal cleaning operations described two plants in Germany.(57) A pilot plant had a capacity of 1.5 tons per hour and operated on a feed sized to 0.1 to 2.0 mm (65 to 150 mesh). The plant had a twin four-roll separator; each roll was 8.2 feet long and 7.5 inches in diameter rotating at 72 rpm. The moisture of the coal had to be reduced from 3 to 1 percent. A 10-ton-per-hour plant was built but did not go into production because of bomb damage during World War II. In the pilot-plant test runs, 72.6 percent of the feed was separated as a 6.2 percent ash coal, while the reject (27.4 percent of feed) was a 36.2 percent ash material.(58) The results demonstrated that although a low-ash-content fraction could be recovered, one-fourth of the coal remained in the high-ash fraction. Such behavior was attributed to the differences in the behavior of the petrographic constituents of coal. Fusain and durain, by virtue of their high carbon content or their greater mineralization, behave as conductors and do not have the capacity of holding a charge to the same extent as vitrain and clarain, both of which are poor conductors. These differences in behavior were compounded by the condition of the surface (i.e., moisture) as well as by the shape and specific gravity of the particles.(57)

The mean values for the removal of pyritic sulfur from 20 German coals evaluated in a laboratory study are given in Table 15.(58) The mean reduction in pyritic sulfur content of the 20 coals was 72 percent. Partial removal of zinc, vanadium, iron, and silicon was inferred since the final ultraclean coal had to produce a coke with less than 0.15 percent of these impurities.

TABLE 15. REMOVAL OF PYRITIC SULFUR BY ELECTROSTATIC SEPARATION(58)
(Mean Results from 20 German Coals)

	Total Sulfur, percent	Pyritic Sulfur, percent
Feed Coal	1.71	0.74
Clean Coal	1.23	0.21
Rejects	3.17	2.14

By using a rotating drum electrifier described by von Szantho(56), coals finer than 0.1 mm (0.06 mm) were separated into fractions with 3.0, 10.5 and 33.5 percent ash, depending on their relative electrical conductivity. The two low-ash fractions contained 59.5 percent of the feed weight.(56)

Drum-type electrostatic separators were used by Gray and Whelan to remove impurities, including pyrites, from low-ranked coals.(59) The size ranges (based on British screen size) were 8 by 16 mesh and 30 by 60 mesh. The sulfur-removal efficiencies given in Table 16 were based on a ratio of the actual removal to that separation possible by float-sink analysis. It was possible to have a high efficiency but poor cleaning if the coal had a low intrinsic washability. Efficiency figures were considered positive when separation was normal, i.e., shale was deflected more than the coal, and negative when behavior was anomalous. It was concluded from the study that pyritic sulfur removal was as efficient as ash elimination. However, the electrostatic method was considered to be no better able to remove finely disseminated sulfur in coal than other physical methods.(59)

TABLE 16. SULFUR REMOVAL FROM LOW-RANK COALS BY ELECTROSTATIC METHODS(59)

Coal	Size Range B.S.S. Screen	Electrode Configuration[(a)]	Cleaning Efficiency, percent	
			Ash	Sulfur
Park No. 6	8 x 16	Corona + graphite roller	+70	+50
Park No. 6	30 x 60	Concave cylindrical electrode	+51	+67
No. 6 + Added Pyrites (1:1)	8 x 16	Trajectory profile electrode	+26	+11
No. 6 + Added Pyrites	8 x 16	Bar and convex electrode	+36	+39

(a) Illustrations given in Reference (59).

Mukai et al.(60), in their study on various sieved fractions between 10 and 35 mesh, showed that the corona-type discharge field was more suited to recovery of a low-ash and low-iron coal concentrate than was separation in a field without a corona discharge when a drum-type separator was used. They also demonstrated that the optimum relative humidity for good separation of Japanese coals was about 60 percent.

More recently, evaluations of the electrostatic method have been done for coals of finer grinds in order to remove the finely disseminated pyrite. Battelle Memorial Institute conducted a study of the behavior of particles of pulverized coal in an electrostatic field. It was hoped that such a study might lead to the development of a process for selectively precipitating pyrite from air-entrained pulverized coal being fed to a boiler.(61) The triboelectric approach was to induce static charges on coal and pyrite particles by rubbing the materials together as they were agitated in an air stream and then effect separation as they flowed past oppositely charged plates. Material collected as positive plate, ground plate, or filter fractions was analyzed. The results for three different coals ground to 50 percent minus 200 mesh are given in Table 17.(61) Approximately half the feed was not precipitated but was collected as a relatively coarse unchanged sample, and about 20 percent was collected as a low-pyrite fraction on the ground plate. Results from experiments using multicycle separations indicated that an unrealistic number of cycles would be necessary to precipitate pyrite selectively from coal.

In a nonuniform electrostatic field separator, inductive charging caused the more conductive pyrite and fusain particles to migrate to the lower-field-intensity side of the device. When a sample of 30 by 200-mesh Illinois No. 6 seam coal was treated in such a device, fractions with progressively increasing pyritic sulfur content were collected at various distances from the high-field side. The results are given in Table 18. The collected fractions produced a 56 percent clean fraction (1.1 percent pyritic sulfur and 4.8 percent ash), a 37 percent middling fraction (3.0 percent pyritic sulfur and 16.3 percent ash), and a 7 percent refuse fractio (13.1 percent pyritic sulfur and 42.4 percent ash). Similar but less encouraging results were obtained for other coals, and one coal could not be separated.(61)

TABLE 17. PERFORMANCE OF TRIBOELECTRIC SEPARATOR ON THREE DIFFERENT COALS (61)

Coal	Fraction	Percent of Total Sample	Pyritic Sulfur(a), percent	Basic Change	Percent Change	Moisture percent	Ash(b), percent
Missouri Tebo Seam	Feed	100	5.5			4.7	27.3
	Filter	54.8	4.0	Decrease	27.4	1.5	27.2
	Ground plate	17.9	2.5	Decrease	54.5	1.0	20.4
	(+) plate	8.6	5.8	Increase	5.5	2.0	53.6
	Uncollected material	18.7	12.6(c)				
Ohio Meigs Creek No. 9 Seam	Feed	100	2.5				13.0
	Filter	52.9	2.0	Decrease	20.0	1.7	13.8
	Ground plate	18.7	1.1	Decrease	56.0	1.4	7.1
	(+) plate	9.6	2.3	Decrease	8.0	1.5	29.8
	Uncollected material	18.8	5.4(c)				
West Virginia Pittsburgh Seam	Feed	100	2.4			0.4	10.4
	Filter	48.3	2.1	Decrease	16.0	0.7	10.1
	Ground plate	23.5	0.8	Decrease	68.0	0.5	5.3
	(+) plate	12.5	4.5	Increase	80.0	0.8	20.9
	Uncollected material	15.7	2.8(c)				

Coal Feeds 50 percent minus 200 mesh

(a) Pyritic sulfur by BCR rapid method
(b) Dry basis.
(c) Calculated

TABLE 18. SEPARATION OF 30 x 200 MESH ILLINOIS NO. 6 SEAM COAL[(a)] IN A NONUNIFORM FIELD ELECTROSTATIC SEPARATOR(61)

Distance from High-Field Side, inches	0-1	1-2	2-3	3-4	4-5	5-6	6-7
Weight, Percent of Samples Collected (b)	38	18	15	10	7	5	7
Pyritic Sulfur, Percent in Sample	1.0	1.3	1.9	2.6	3.7	6.0	13.1
Ash, Percent in Sample	4.4	6.1	9.2	13.5	17.2	22.4	42.4

(a) Feed material: 3.2 percent pyritic sulfur, 14.5 percent ash.

(b) Material balance not made since losses occurred throughout the equipment.

In the dry separation process for pyrite removal from coal reported by Abel, et al.(10,11,62), the air classification was augmented with the use of electrostatic separation, as shown in Figure 6. The process is intended to be used for removing pyrite from coal ground to 75 percent minus 200 mesh before use in power generation plants. The electrostatic separator shown schematically in Figure 7 was evaluated with blends consisting of 90 percent coal and 10 percent pyrite in the size ranges 80 by 100 mesh and 270 by 400 mesh. The results of the evaluation are given in Table 19. Sharper separations were obtained with the coarser fraction since less middlings were accumulated.

The performance of the combined air classification and electrostatic separation on Pittsburgh-seam roof coal is most effective when cleaning is carried out between stages of grinding. The results given in Figure 8 show that 35 percent of the total pyritic sulfur was removed after the first stage, with an additional 12 percent being removed after the remaining grinding stages. Although only about 47 percent of the total pyritic sulfur was removed, this amounted to about 90 percent of the available pyritic sulfur determined by float-sink analysis.(62) Without staged grinding, 30 to 50 percent of the total pyritic sulfur (amounting to 50 to 70 percent of available pyritic sulfur) was removed with rejects of 10 to 15 percent. It was concluded that since both centrifugal and electrostatic separations are benefited by restricting particle-size range and by maintaining the pyrite particles as large as possible, the efficiency of pyrite removal is improved by integrating grinding with the separation process, i.e., staged grinding.

2.1.6 Separation Methods Based on Magnetic-Property Differences

Coal minerals have not been generally considered magnetic and, therefore, were not believed to be amenable to magnetic separation. However, enhancement of the magnetic properties of the minerals can be brought about through low-temperature oxidation, thermomagnetic treatment of coals at low temperatures and high fields, phase changes brought about at high temperatures, treatment in steam, and high-frequency dielectric heating. Removal

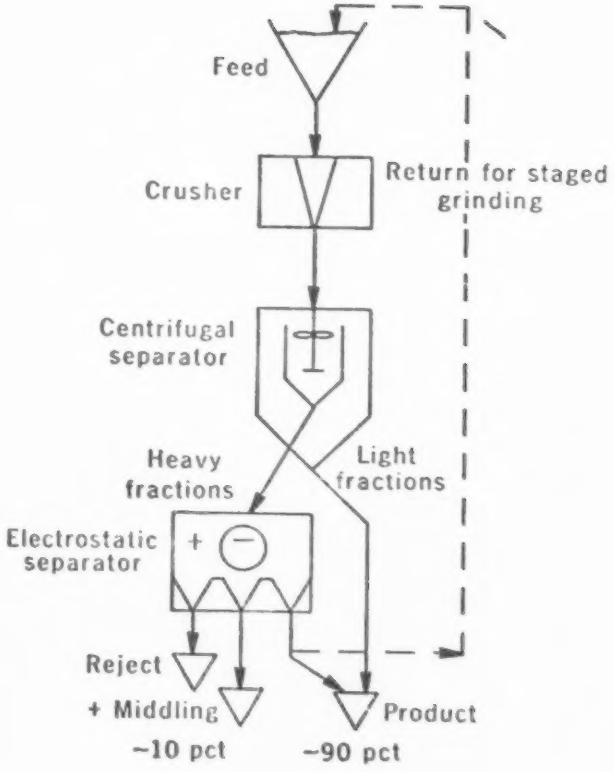

Feed
Crusher
Return for staged grinding
Centrifugal separator
Heavy fractions
Light fractions
Electrostatic separator
+
Reject
+ Middling
~10 pct
Product
~90 pct

FIGURE 6. DRY PROCESS FOR REMOVAL OF PYRITE FROM COAL(62)

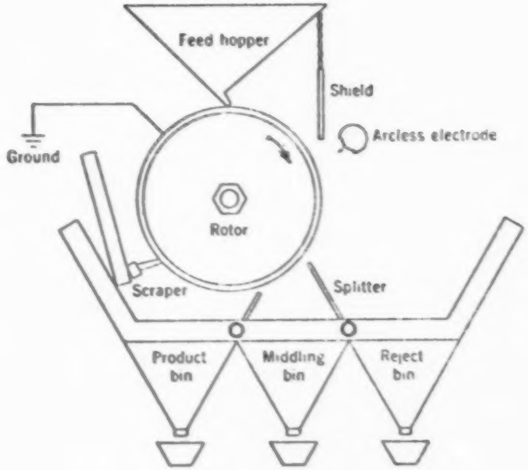

Feed hopper
Shield
Arcless electrode
Ground
Rotor
Scraper
Splitter
Product bin
Middling bin
Reject bin

FIGURE 7. ELECTROSTATIC SEPARATOR(62)

TABLE 19. ELECTROSTATIC SEPARATION OF CLOSELY SIZED BLENDS CONSISTING OF 90 PERCENT COAL AND 10 PERCENT PYRITIC MATERIAL(62)

Component	Distribution of Each Component, percent Reject	Middling	Product
	80 x 100-mesh blend		
Coal[(a)]	2.7	0.3	97.0
Pyritic material[(b)]	97.8	0.4	1.8
	270 x 400-mesh blend		
Coal[(a)]	1.8	6.2	92.0
Pyritic material[(b)]	97.9	2.0	0.1

(a) Coal from Kittanning seam, comprising 90 percent of blend, previously cleaned by removing sink at 1.6 sp gr.

(b) Pyritic material from Pittsburgh seam, comprising 10 percent of blend, previously cleaned by removing float at 2.89 sp gr.

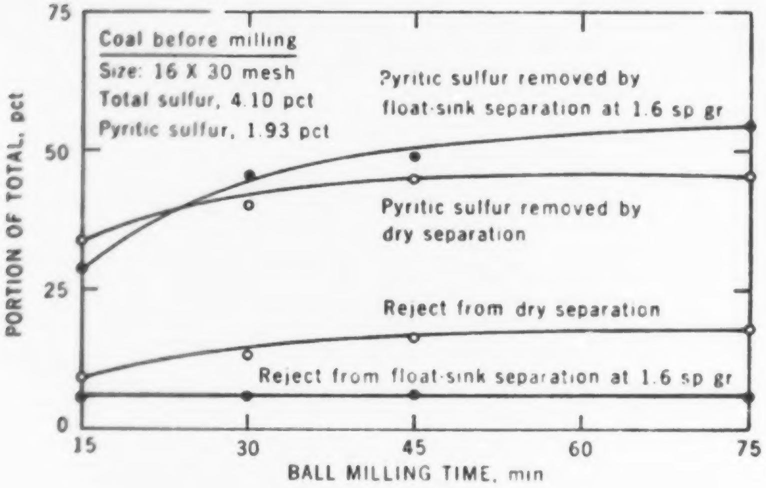


FIGURE 8. COMBINED CENTRIFUGAL-ELECTROSTATIC SEPARATION OF PYRITE FROM PITTSBURGH SEAM ROOF COAL WITH STAGED GRINDING(62)

of ash minerals and pyrite in untreated coal has been demonstrated, which indicates that paramagnetic as well as ferromagnetic materials might be removed by magnetic methods. The methods summarized in Table 20 are discussed further in this section.

Recent reviews(63,64) point out that the concept is not new, and the earliest published work in the reduction of sulfur in coal by magnetic means was a description in a German patent issued in 1957 which was issued as an addition to a U.S. patent issued in 1956.(65) These patents disclosed that when superheated steam (200 to 300 C) was used to distill resins from a coal sample, the pyrite was reduced to FeS. With the addition of an alkali or alkaline-earth hydroxides or carbonates during treatment, FeS could be separated magnetically.

Yurovsky et al.(66) reported that during treatment-of Russian coals with superheated steam and air, the surface of the pyrite in coal underwent thermochemical reactions to form films of magnetite, hematite, and pyrrhotite. After this treatment, a reduction of 32 percent in total sulfur was achieved in the 1 mm x 0 fraction by magnetic separation. The coal yield was about 84 percent.

In a laboratory evaluation of the concept, Kester(67) was able to demonstrate both ash and sulfur reduction after treatment with steam and air at temperatures between 196 and 271 C for periods of 5 to 10 minutes. The reduction in sulfur was between 15 and 79 percent for coals in the 100 to 150 mesh size range (see Table 21). What was more significant in Kester's study was that comparable ash and sulfur removal was possible with coals that were not thermally treated. The magnetic field used for the separations of treated and untreated coals was identical at 10,700 gauss, which is considered to be a high-intensity field (e.g., a Frantz separator used in mineralogical studies). In a later study, Kester et al. evaluated the concept of magnetic separation of minerals from untreated pulverized coal from three other sources with the minus 200-mesh portion removed (i.e., 48 by 200 mesh).(68) The results of the study are summarized in Table 22. The removal of sulfate sulfur was attributed to the magnetic susceptability readily measured for the pure substance. Values for the magnetic susceptibilities for some of the mineral impurities of coal are

TABLE 20. SEPARATION METHODS BASED ON MAGNETIC-PROPERTY DIFFERENCES

Pretreatment	Typical Feed Size	Status of Use	Contaminants Removed and Performance	Reference
Thermochemically treated (steam and air)	100 to 150 mesh	Experimental	Ash, 27 to 55% removed Sulfur, 15 to 79% removed	67
Thermally treated				
>500 C	?	Experimental	Pyrite	70
Microwave heating	?	Experimental	Pyrite	
Unheated coal	Minus 48 to 200 mesh	Experimental	Ash, 26 to 45% removed Sulfur, total, 29 to 62% removed Sulfur, pyritic 54 to 83% removed Sulfur, organic, 5 to 29% removed Sulfur, sulfate, 62 to 81% removed	68
	Minus 100 mesh	Experimental	Pyritic sulfur, 7 to 60% removed	70

TABLE 21. REMOVAL OF SULFUR FROM UPPER FREEPORT COAL BY MAGNETIC SEPARATION[a] WITH AND WITHOUT THERMAL TREATMENT (100 by 150 MESH)(67)

Prior Treatment	Raw Unheated Feed Average, percent		Coal Recovery, percent	Reduction in Ash, percent	Reduction in Sulfur, percent
	Ash	S			
Thermally treated (196 to 271 C 5 to 10 min)	19.30	3.07[b]	77.2 to 88.9	26.71 to 55.85	14.7 to 78.8
None	19.26	2.98	88.08	34.23 avg.	51.66 avg.

(a) Magnetic field flux density: 10,700 gauss.

(b) Coal feed rate 12.6 g/hr.

TABLE 22. REMOVAL OF SULFUR AND ASH BY MAGNETIC SEPARATION OF VARIOUS UNTREATED COALS (MINUS 48 by 200 MESH)(68)

	Removal, percent				
		Sulfur Forms			
Coal Seam Samples	Ash	Pyritic	Organic(a)	Sulfate	Total Sulfur
Upper Freeport	38	83	29	74	62
Redstone	26	54	5	62	29
Swickely	45	65	17	75	42
Pittsburgh	42	86	25	81	60

(a) Authors were unable to explain reduction in organic sulfur based on magnetic characteristics of organic materials cited on the next table.

given in Table 23. If the values are positive, the material is paramagnetic (or attracted further into the magnetic field); if they are negative, the material is diamagnetic (or are forced out of the magnetic field). In the light of these values, the authors were unable to explain the reductions observed in organic sulfur after magnetic separation treatment.

The removal of mineral components, especially pyrite, from an aqueous suspension of finely ground coal has been demonstrated on a laboratory scale by Trindade et al,(69) using the concept of a high-gradient magnetic separator operating at a field intensity of 20,000 oersteds. The results shown in Table 24 were typical of those obtained during the laboratory studies. Both the minerals and pyritic sulfur were removed. The schematic of the arrangement of the experimental device is shown in Figure 9. The separator consisted of a column packed with either magnetic stainless steel wool or screen which was inserted in the bore of a solenoid magnet. The void space within the column was usually about 90 percent. The coal was ground to top sizes of 0.42 mm down to 0.044 mm and used to prepare slurries with a concentration of about 2.5 percent. The slurry linear velocity through the packed bed was about 2.3 to 2.6 cm/sec. Their model for the forces acting on a pyrite particle during the separation (i.e., magnetic force opposed by the weight and hydrodynamic drag of the particle) allowed them to predict that there should be a given size particle for which the action of the magnetic forces is maximized for a given stream velocity. The experimental results shown in Figure 10 supported this model very well. At higher linear velocities, they showed that the majority of the material remaining in the separator would be the more highly susceptible pyrite. Trindade et al. believed that the enhancement of the magnetic susceptibility of the pyrite by chemical or thermal treatment prior to separation and the use of an air suspension of coal were reasonable areas for future research.(69) They also recommended further studies into the magnetochemistry of pyrites.*

Ergun and Bean(70), in a separate study, showed that pyritic sulfur removal could be accomplished by magnetic separation without pretreatment using an induced-roll magnetic separator. Seven coals pulverized to minus 100 mesh were evaluated and coal recoveries ranged from 60 to 87 percent. In two of the coals, about 60 percent of the pyrite could be removed, while

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* Programs in these areas are now ongoing.

TABLE 23. MAGNETIC CHARACTERISTICS OF COAL COMPONENTS (68,69)

Component	Magnetic Susceptibility, 10^{-6} emu/g
Organic material	-0.4 to -0.8
Shales	+39 to 45
Kaolins	+20 to 39
Sandstone	15 to 20
Sulfides	+3 to 120
Pyrite FeS_2	4.53 to 120
Marcasite FeS_2	5.43
Carbonates	-0.4 to +100
Siderite ($FeCO_3$)	3.8
Limestone	0.75
Calcite ($CaCO_3$)	
Chlorides	-0.9 to -1.3
Sulfates	
Ferrous sulfate	
$FeSO_4$	74.2
$FeSO_4 \cdot 7H_2O$	41.5
Ferric sulfate	
$Fe_2(SO_4)_3$	57.3
Calcium sulfate	
$CaSO_4$	-0.364
$CaSO_4 \cdot H_2O$	-0.384
Aluminum sulfate	
$Al_2(SO_4)_3$	-0.48
Magnesium sulfate	
$MgSO_4$	-0.45
$MgSO_4 \cdot 7H_2O$	-0.551

TABLE 24. TYPICAL RESULTS OF LABORATORY TEST OF HIGH-GRADIENT MAGNETIC SEPARATION OF IMPURITIES FROM COAL(69)

	Recovery, percent	Composition, percent			Reduction, percent		
			Sulfur			Sulfur	
		Ash	Total	Pyritic	Ash	Total	Pyritic
Feed(a)	-	27.0	1.32	0.66	-	-	-
Cleaned Coal	80.8	24.0	0.81	0.24	11.1	39.7	63.7
Magnetic Refuse	14.4	38.9	2.52	2.01	-	-	-

(a) Coal size: 0.044 mm or less.

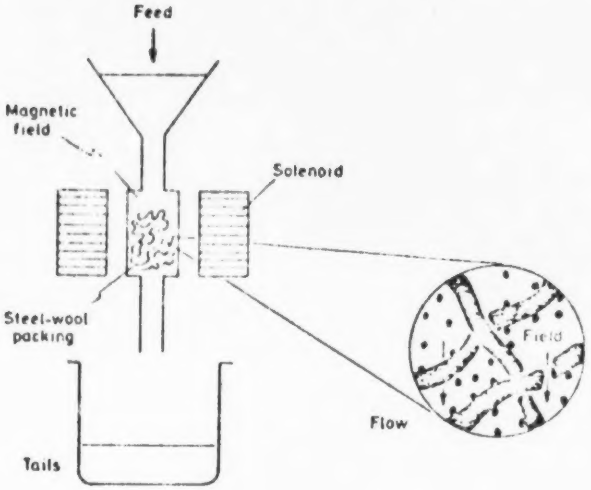

Feed
Magnetic field
Solenoid
Steel-wool packing
Field
Flow
Tails

FIGURE 9. SCHEMATIC OF EQUIPMENT USED FOR HIGH-GRADIENT MAGNETIC FIELD SEPARATION STUDIES(69)

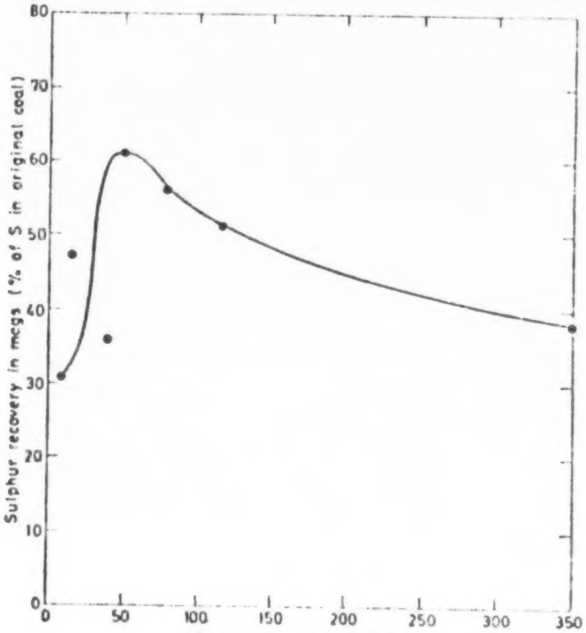


FIGURE 10. OBSERVED EFFECT OF PARTICLE SIZE ON SULFUR RECOVERY IN MATERIAL ISOLATED IN MAGNETIC FIELD (MAGS)(69)

in the other five, the removal ranged from 7 to 44 percent. The poorest performance was obtained for the Upper Freeport coal-seam sample, which is in contrast to the results obtained by Kester et al.(68)

Ergun and Bean(70) established that crushing did not enhance the magnetic susceptibility of pyrite but disclosed that weathering enhanced the sulfur removal by magnetic separation owing to the formation of iron sulfate salts. Thermal treatment that also oxidized the pyrite to iron sulfate also enhanced removal. Thermal treatment alone, unless the pyrite is heated to >400 C, has only marginal effect. Heating to temperatures above 500 C will cause a rapid and sufficient conversion of pyrite to pyrrhotite in 1 second or less and makes magnetic separation possible. The trick was to do it without heating the coal. To this end, Ergun and Bean investigated both induction and dielectric heating in the radio and microwave frequency range and found that pyrite could be heated rapidly upon exposure to microwave radiation at the 2450 MHz and 10 GHz frequency bands. The potential of the concept is that the pyrite can be heated in the coal matrix without crushing since the coal and nonpyrite minerals are not heated as rapidly. Ergun and Bean infer that the individual particles of pyrite dispersed in coal would attain a temperature of >500 C, while the coal itself would not be heated by the microwaves but only by conduction from the hot pyrite particles. The authors have had patents issued on the process which state that the size range of coal preferred is 0.034 to 0.074 mm, and microwave radiation between 400 kHz and 10,000 MHz could be used.(71,72) Although the pyrite conversion is thermochemical, the actual separation of the pyrite is done magnetically.

2.1.7 Commercial Coal Preparation Practice

Preparation of run-of-mine coal for fuel consumption as practiced on a commercial scale is becoming more important and difficult as coals become finer, dirtier, and wetter. It is further complicated by the specifications demanded by the market and the environmental concerns about waste disposal. Typical commercial coal preparation plants are designed to handle many qualities of raw coal and they incorporate many of the methods discussed individually in this section on physical methods of contaminant removal. How these methods fit together for maximum coal recovery and contaminant removal may best be described with two illustrations of modern facilities.

As an example of the type of operations that are involved in a modern coal-cleaning plant, a schematic flowsheet of a recent design of a plant is given in Figure 11.(73) Incoming raw coal is crushed to a top size of 5 inches. An initial size separation of 1/4 inch x 0 fraction is achieved over double-decked screens. The 5 inches x 1/4 inch fraction is sent to heavy media vessels wherein at least a 99 percent recovery of the coal (Btu basis) is possible after separation from the waste. Then a double-decked screen effects a separation of the 5 inches x 1-1/4 inches and 1-1/4 inch x 1/4 inch fractions. The former is crushed to a top size of 1-1/4 inch while the latter is centrifuged.

These two streams are combined and sent to the load-out facilities. The 1/4 inch x 0 size range resulting from the initial separation is separate into two fractions (1/4 inch x 28 mesh and 28 mesh x 0) using sieve bends and vibrating screens. Separation of waste from the 1/4 inch x 28 mesh is achiev in heavy-media cyclones. Froth flotation is used for the 28 mesh x 0 fracti Dewatering by centrifugation is employed for the first fraction while a disk-type vacuum filter is used for the second. Both fractions are combined and finally dried in a coal-fired fluidized bed dryer. The dryer exhaust is then sent through a cyclone and a Research-Cottrell flooded disk, high-energy venturi for control of particulates.

The plant is designed for closed-loop operation. Make-up water is needed mainly for losses in the thermal dryer. A slurry of magnetite in water is the heavy medium employed. Elaborate schemes are employed for recovery and conservation of the magnetite. The circuit for this purpose consists of (1) a sump wherein the dilute medium collects, (2) classifying cyclones for separation of a concentrated slurry, (3) a magnetite thickener the same purpose as (2) above, and (4) a magnetic separator for separation of magnetite from waste.

Another example of a coal preparation plant is given in Figure 12.(3,74) Although no material balance is given, it does illustrate the combination of processes necessary for high coal recovery and effective contaminant removal. There is no standard flow sheet for dense medium cleaning with a magnetite medium. Each plant is tailored to produce a specified product from a raw coal having specific washability characteristics.

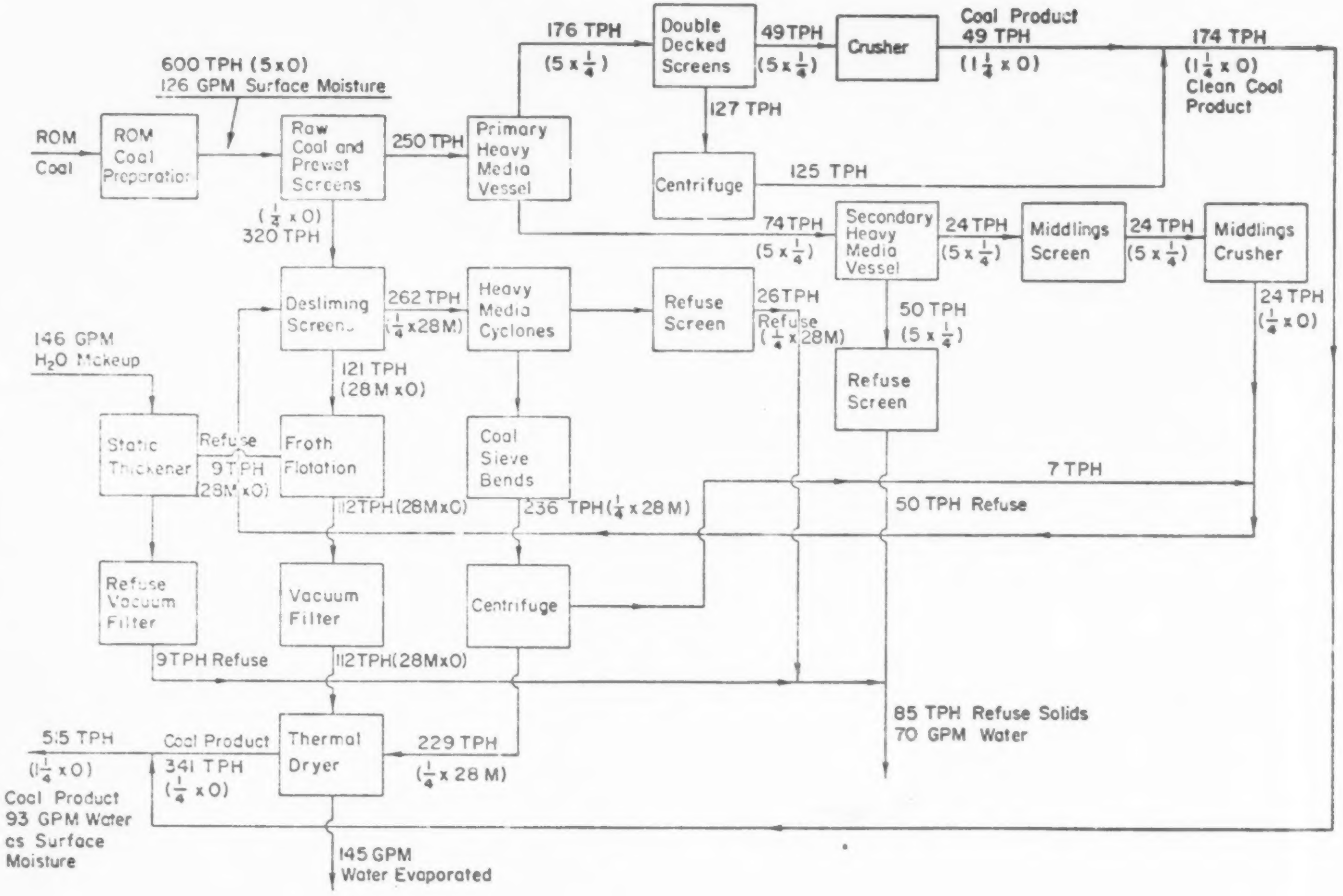

ROM
Coal
ROM Coal Preparation
600 TPH (5 x 0)
126 GPM Surface Moisture
Raw Coal and Prewet Screens
250 TPH
($\frac{1}{4}$ x 0)
320 TPH
Primary Heavy Media Vessel
176 TPH
(5 x $\frac{1}{4}$)
Double Decked Screens
49 TPH
(5 x $\frac{1}{4}$)
Crusher
Coal Product
49 TPH
(1$\frac{1}{4}$ x 0)
174 TPH
(1$\frac{1}{4}$ x 0)
Clean Coal Product
127 TPH
Centrifuge
125 TPH
74 TPH
(5 x $\frac{1}{4}$)
Secondary Heavy Media Vessel
24 TPH
(5 x $\frac{1}{4}$)
Middlings Screen
24 TPH
(5 x $\frac{1}{4}$)
Middlings Crusher
24 TPH
($\frac{1}{4}$ x 0)
Desliming Screens
262 TPH
($\frac{1}{4}$ x 28M)
Heavy Media Cyclones
Refuse Screen
26 TPH
Refuse
($\frac{1}{4}$ x 28M)
50 TPH
(5 x $\frac{1}{4}$)
Refuse Screen
146 GPM
H_2O Makeup
Static Thickener
Refuse
9 TPH
(28M x 0)
121 TPH
(28M x 0)
Froth Flotation
Coal Sieve Bends
112 TPH (28M x 0)
236 TPH ($\frac{1}{4}$ x 28 M)
7 TPH
50 TPH Refuse
Refuse Vacuum Filter
Vacuum Filter
Centrifuge
9 TPH Refuse
112 TPH (28M x 0)
85 TPH Refuse Solids
70 GPM Water
5:5 TPH
(1$\frac{1}{4}$ x 0)
Coal Product
93 GPM Water as Surface Moisture
Coal Product
341 TPH
($\frac{1}{4}$ x 0)
Thermal Dryer
229 TPH
($\frac{1}{4}$ x 28 M)
145 GPM
Water Evaporated

FIGURE 11. SCHEMATIC FLOW DIAGRAM WITH APPROXIMATE MATERIAL BALANCE OF A 600 TPH METALLURGICAL COAL CLEANING PLANT(73)

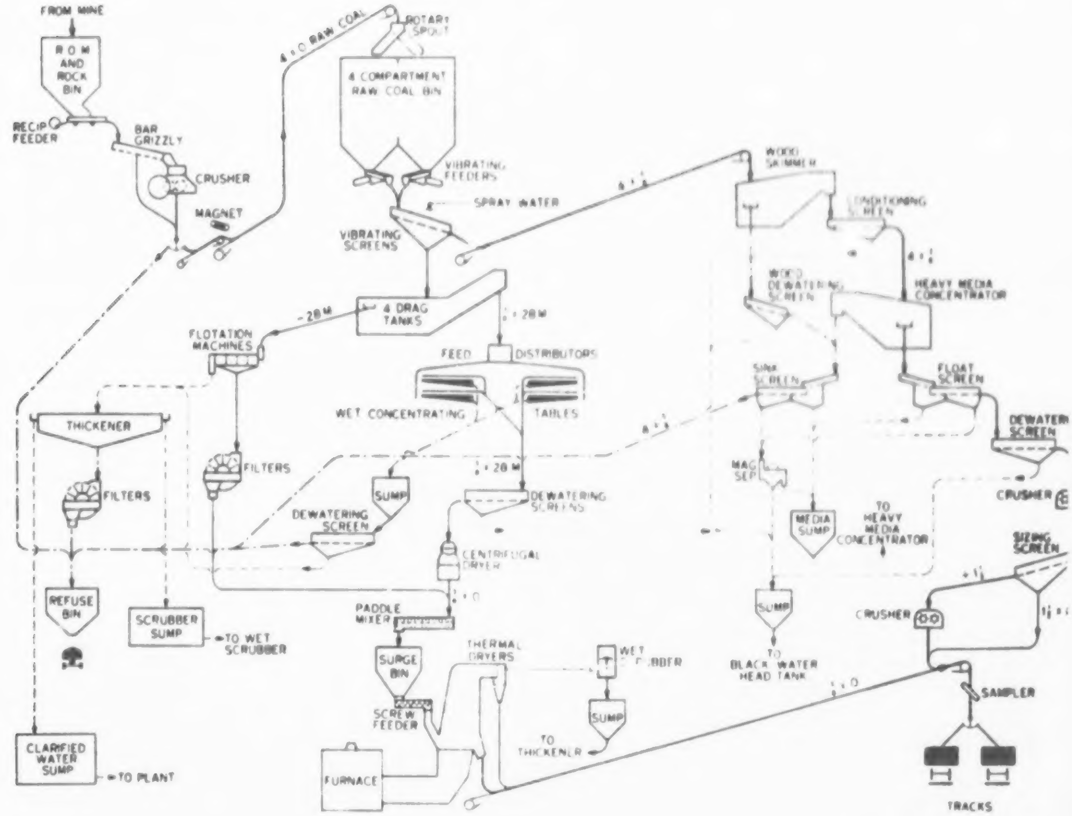

FROM MINE
R O M AND ROCK BIN
RECIP FEEDER
BAR GRIZZLY
CRUSHER
MAGNET
4 x 0 RAW COAL
ROTARY SPOUT
4 COMPARTMENT RAW COAL BIN
VIBRATING FEEDERS
SPRAY WATER
VIBRATING SCREENS
WOOD SKIMMER
CONDITIONING SCREEN
WOOD DEWATERING SCREEN
HEAVY MEDIA CONCENTRATOR
4 DRAG TANKS
-28 M
+28 M
FLOTATION MACHINES
FEED DISTRIBUTORS
WET CONCENTRATING TABLES
SINK SCREEN
FLOAT SCREEN
DEWATERI
SCREEN
THICKENER
FILTERS
FILTERS
SUMP
DEWATERING SCREEN
DEWATERING SCREENS
+28 M
MAG SEP
MEDIA SUMP
TO HEAVY MEDIA CONCENTRATOR
CRUSHER
SIZING SCREEN
CENTRIFUGAL DRYER
REFUSE BIN
SCRUBBER SUMP
TO WET SCRUBBER
PADDLE MIXER
SURGE BIN
SCREW FEEDER
THERMAL DRYERS
WET SCRUBBER
SUMP
TO THICKENER
SUMP
TO BLACK WATER HEAD TANK
CRUSHER
SAMPLER
CLARIFIED WATER SUMP
TO PLANT
FURNACE
TRACKS

FIGURE 12. TYPICAL THREE-PROCESS PLANT EMPLOYING DENSE MEDIUM FOR COARSE COAL CLEANING(3,74)
Source: U.S. Bureau of Mines

2.2 Carbonization/Pyrolysis Methods of Contaminant Removal

Carbonization or "dry" distillation of coal(75-78) is the heating of coal in the absence of air and is practiced in industrial size units. The primary object is to make either solid coke or a low-Btu gas (150 to 250 Btu/ft^3). During the last decade, fluidized bed pyrolysis processes that make liquids from coal have been developed.

The primary objective of coal carbonization is the production of coal for blast furnaces. When a low-Btu gas is produced, the coke production is considered as a by-product. The heating of coal tends to concentrate and thus separate the carbon and the inorganic matter from the gaseous matter and liquid condensates obtained therefrom. The products of coal carbonization are given in Table 25.

TABLE 25. PRODUCTS OF COAL CARBONIZATION(79)

U.S. Production of Crude Tar, million gal (1968)	750
Used as Fuel	104
At Least Partially Processed	644
From 1 ton of coal (Average values):	
Coke, lb	1,500
Coke-Oven Gas, scf	11,000
Tar, gal	10

The term pyrolysis has recently been used for improved processes (e.g., Clean Coke) being developed for coke production. Frequently, pyrolysis, as referred to in the coal industry, means heating of coal in small laboratory-size units with the objective of studying fundamentals of decomposition and related subjects, e.g., kinetics of gas evolution.

The thermal decomposition reactions of coal are more favorable to the enrichment of most of the minor elements in the residue than is combustion. This is due primarily to the strongly reducing conditions in coke and low-Btu gas production. Some of the minor elements appear to be associated with the organic matter since they are extracted with organic matter and distill over with tars.

As coal is heated, various changes take place, ranging from mild depolymerization to extensive cracking. During heating of coal in a vacuum, it is observed that no distillation occurs until such temperatures are reach that there is definite evidence of thermal decomposition.(77) The loss of sulfur and nitrogen contaminants and certain trace elements, e.g., mercur and arsenic, thus occurs, due partially to decomposition reactions and partially to the high volatility of the contaminants. As discussed in the separate coal contaminant characterization volume of this study, the contaminants (except pyrites and some other discrete minerals) in coal are present as an integral part of the coal structure such that a certain amount of coal decomposition would have to occur before the contaminant could be removed from the coal.

In coal carbonization it is found that the yield of tar becomes a maximum at 500 to 600 C but decreases at higher temperatures owing to the degradation of the initial primary products, as shown in Figure 13. The gas yields from carbonization are thus inversely related to tar (liquid) yields. Gas from low- and high-temperature operations contains ammonia and sulfur compounds which are formed mostly from the decomposition of organic and some inorganic compounds. The liquid products contain pyridine, carbazoles, thiophene, benzothiophene-type contaminants, and trace elements. Processes in which a maximum coal temperature of up to 700 C is reached are normally considered as low-temperature processes. The high-temperature processes operate at over 900 C. Some of the significant processes, past and present, are described in Table 26. This table also shows the distribution of the contaminants as the coal goes through the different carbonization processes.(83-89)

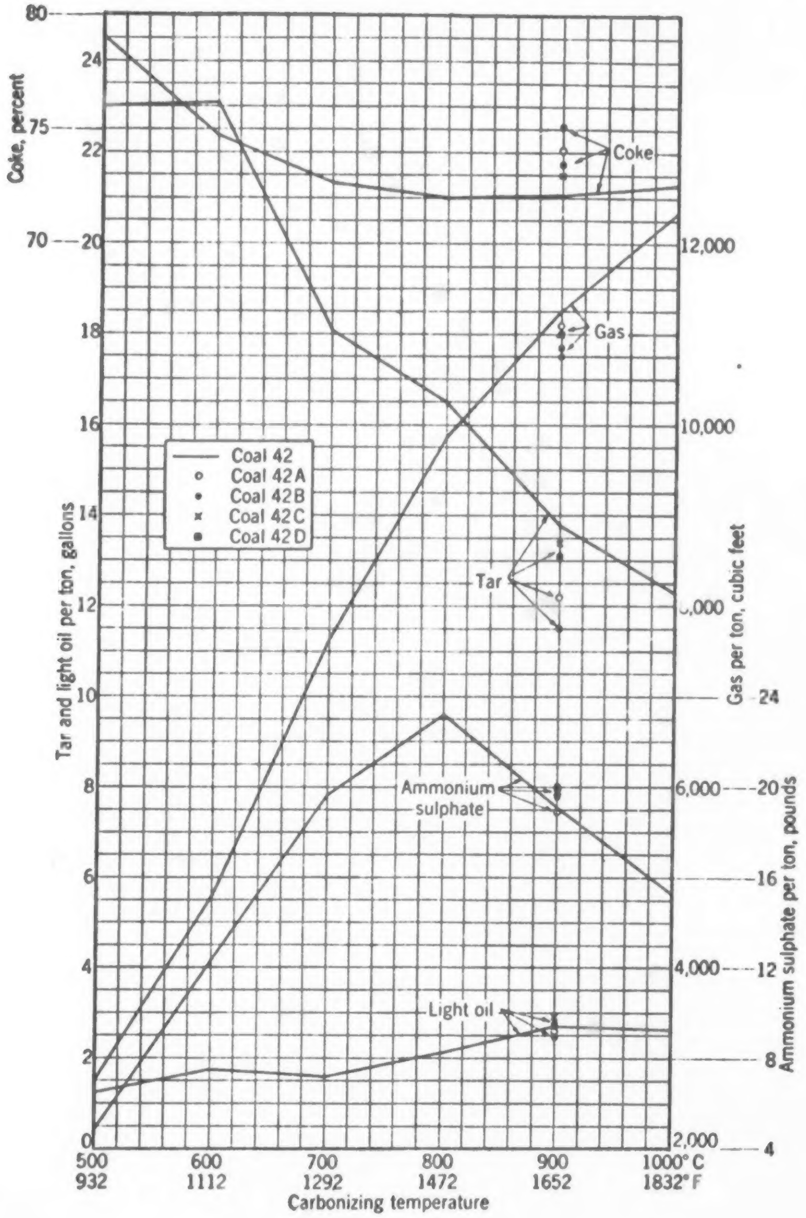


FIGURE 13. YIELDS OF CARBONIZATION PRODUCTS FROM UPPER BANNER SEAM COAL(80)

TABLE 26. COAL CARBONIZATION/PYROLYSIS PROCESSES

Process	Process Developer, Status	Objective	Process Description	Distribution of Contaminants in Products
Recent Processes				
Char Oil Energy Development (COED)(83)	FMC, Princeton developed since 1962, 36 tons/day pilot plant processed 18,000 tons coal in 1974 Estimate for 24,000 tons of clean coal available.	Maximize liquid production from coal by pyrolysis.	Multistage fluidized-bed pyrolysis of coal. Catalytic hydrotreating of the oil yields synthetic crude suitable as petroleum refinery feedstock. The product gas can be used as boiler fuel or for gasification. Four fluidized-beds temperature from 316-816 C, char 59.5%, oil 19.3%, gas 15.1%, liquor 6.1% based on Illinois No. 6 coal.	The low temperature of pyrolysis will concentrate the trace elements and N, S compounds in the char. The liquid product contains S, N which are removed by hydrotreatment.
COALCON(83) (Hydrocarbonization)	Union Carbide, Chemico. 2600 tons/day high sulfur coal const. of demo. plant announced Nov. 1975,3900 bbl liquid fuel and 22 MM scf SNG/day	Produce liquids and gas	Sized, dried and preheated coal is fed to a dry, fluidized-bed hydrogenation reactor. Hot vapor products separated. The char from the hydrogenator is gasified. (No process conditions available)	First stage hydrogenation would remove S, N to some extent depending on process conditions. Depending on the gasifier operating conditions the trace elements would appear in the product gases. (Postulated)
Clean Coke(83,86)	U.S. Steel 1972 500 lb/day PDUs. 100 TPD next.		Detailed designs of PDU's on: (1) Coal and coke preparation (2) Carbonization (3) Hydrogenation (4) Slurry oil preparation (5) Binder preparation. Coal after beneficiation split into two fractions. Portion of coal carbonized and desulfurized to produce met. coke. The rest of coal slurried with process derived oil and hydrogenated carbonization 649-760 C, extraction hydrogenation 482 C.	A closed process with no significant emissions. The liquid produced desulfurized by hydrogen treatment. The char contains 0.5% S versus 1.74% for coal
Cogas(83)	Cogas Develop Co., Princeton. 2.5 TPD and 50 TPD pilot plants being operated. Planning 800-1000 TPD.		Variation of COED process Gasifier-Combustor, 816-927 C. Med-Btu gas cleaned of S.	The char when gasified at the high temperatures will lead to trace elements in the gas stream. (Postulated) The liquid is desulfurized by hydrogen treatment.
Carrett's(83, 84) Coal Pyrolysis	Occidental Pet. Corp. 3.6 TPD pilot plant being tested.		Crushed coal is introduced into the pyrolyser in a stream of recycle gas and is pyrolysed at 593 C through contact with hot char, 649-841 C. Part of product gas reformed for hydrogen to hydrotreat tar. Yields,char 56.7%, tar 35%, gas 6.5%, 1.8% water.	Desulfurization of char by acid treatment proposed. The trace elements will concentrate in the char.
Seacoke(83)	Arco Chem. Co. Project sponsored in 1960s (COED has replaced this process.)	Liquid, char and gas	Process conditions not available.Coal usually blended with petroleum residium as part of feedstock, subjected to multistage fluidized bed pyrolysis.	The trace elements in pet. residium and coal could concentrate in the char (Postulated). The liquid fraction was hydrotreated.
Carbonization(85) of Lignite to motor fuels	Noel, H. M. U.S. Patent 2,676,908 4/27/54.	Low grade coals to liquids, char gas	"Methalation" technique using 2 to 6% calcium acetate, sodium carbonate, iron filings, carbonization at 760-1093 C.	The trace elements would appear in gas and in ash (postulated). H_2S is found in the gas.
Fractional Carbonization of coal (85)	Eddinger, R.T., et. al., U.S. Patent 3,574,065 [Inventor of COED]	Liquids gas	Staged pyrolysis and finally combustion	Fate of trace elements as in any carbonization study

TABLE 26. Continued

	Process Developer, Status	Objective	Process Description	Distribution of Contaminants in Products
Pyrolyzing of solid or liquid fuel(85)	A.M. Squires U.S. Patent 3,597,327 8/31/71	Gas and char	Two-stage fluidized-bed pyrolyser, the heat supplied to the lower zone by conduction from the top zone. The lower bed carbonizer is at 760 C and the top one at 949 C. Dolomite is used to remove the sulfur.	Fuel gas and coke products free of sulfur are produced. The fate of trace elements is not mentioned. (They would end up in coke pellets - postulate)
COMMERCIALLY DEVELOPED "OLD" PROCESSES				
Low Temperature Carbonization				
DISCO(80)	Disco Co. was installed near Pittsburgh in the 50s.	Coke, tar,gas	Designed for certain coals. Bituminous coal ground to 3/8 in size, heated in a revolving steel retort. The carbonizer gas is at 450-480 C.	The low temperature of operation does not remove any contaminants. Feed coal had 2.2% S, and coke produced had 2.1% S.
Hayes Process(80)	Allis-Chalmers was operated at Moundsville, W.A. in the 50s.	Coke, tar, gas	Rotating tube retort with a screw conveyor. The temperature at feed end was 595-705 C. The gas had a heating value of 939 Btu/ft^3.	Coke contained 3.5% ash compared to 9.85% for coal.
Krupp-Lurgi(79,80) Process	Developed in 30s. Only large scale plants in Germany	Coke tar,gas	Oven consisted of six carbonization cells, entering gas was at 620 C and exit gas at 570-580 C.	The ash content of coke was 3.8% versus 5.4% for coal. The gas contained 6% nitrogen.
Brennstoff-Technak Cellon Jones Oven Carmaux Oven Otto Retort Weber Process Phurnacite Process Parker Retort(78)	Processes developed for specific coals e.g., slightly caking	coke	Fixed-bed operation.	The temperatures controlled contaminant removal from the coke.
Rexco Process(78)	Developed and operated in England.	coke, tar,gas	The directly heated fixed bed retorts were operated at 700 C.	Rexco coke had 7.2% ash versus 4.9% for coal.
Koppers(78)	Developed in Germany.	Coke, tar,gas	Continuous vertical retort, for non-caking coals. Temperatures of 800-1000 C attained.	Higher temperatures would remove S, N, trace metal contaminants from the coke.
Parry Process(78)	Developed U.S.Bureau of Mines	Coke, tar,gas	Entrained Carbonization, temperatures of 1038 C.	With fine particle size of feed coal and high operating temperatures S, N, trace elements removal from coke possible.
High Temperature Carbonization				
Koppers(78,87) (includes Becker)	Koppers	Coke, tar,gas	Cross-regenerative by-product oven.	Depending on the temperature the S,N, trace metal contaminants can be concentrated in the coke or liquid or gas products.
Wilputte(78,87)	Wilputte	Coke, tar,gas	Vertical flue oven.	
Semet-Solvay(78,87)		Coke, tar,gas	Horizontal heating flues.	
Otto(78,87)		Coke, tar,gas	Vertical flue oven.	
Beehive(87)	The original coke oven	Coke, tar,gas	Carbonization occurs in the partially open oven	The product gases are allowed to escape.

2.2.1 Sulfur Contaminants(80)

The sulfur is distributed among the carbonization products in the following approximate proportions:

	Percent Distribution
Coke	50-65
Gas, as hydrogen sulfide or carbon disulfide	25-30
Thiophene and other organic compounds	1-15
Tar and ammonia liquor	balance

Hydrogen sulfide and other sulfur compounds in the volatile products begin to form in quantity around 250 C, but the reactions which produce them are probably largely completed in the temperature range 500 to 800 C. Both the sulfur combined in the coal substance and that in the mineral matter (pyrites, sulfates) of the coal contribute to the formation of volatile sulfur compounds. No pyrite is converted to FeS.(80)

Blends of complex sulfur compounds (dyes) and materials like starch or Bakelite, as given in Table 27, were pyrolyzed at 625 C to determine the distribution of the sulfur in the product gases and that in the residue.(81) The percentage of sulfur retained in the Wyoming char, in the Robena coal, and in the other mixtures is shown in Figure 14, where P_T, a factor based on the probability of H_2S formation, is correlated to sulfur retention in the residue. It was found that up to 85 percent of the sulfur was retained in the residue of the Wyoming char and 45 percent in that for Robena coal.

2.2.2 Nitrogen Contaminants(80)

The nitrogen of coal is commonly distributed among the high-temperature carbonization products as:

	Percent Distribution
Coke	40-60
Ammonia	10-20
Hydrogen cyanide	1-2
Tars, pyridine, quinoline	1-4
Nitrogen gas	balance

TABLE 27. DATA ON PYROLYSIS OF BLENDS OF MODEL COMPOUNDS (81)

Blend	Composition, atom %				Volatile Matter, wt %	Sulfur Retained, wt %	$P_T (10^3)$
	C	H	O	S			
1.0 Dye[a]	37.7	41.7	19.6	1.13	67	67	0.53
2.0 Starch 0.1 Dye	29.4	47.5	23.4	0.11	73	100	0.06
2.9 Starch 1.0 Dye	53.8	37.4	7.55	1.14	37	67	0.98
2.0 Bakelite 0.1 Dye	47.3	45.7	6.72	0.10	37	76	0.15
2.9 Bakelite 1.0 Dye	30.5	66.7	1.88	0.91	70	13	3.76
2.0 Naphthene 0.1 Dye	35.8	64.2	0.13	0.07	67	3	0.28
2.9 Naphthene Robena Coal[b]	53.4	42.6	3.64	0.28	29	46	0.12
3738-118-1 Wyoming Char	58.5	31.1	10.2	0.18	53	85	0.04
3940-64-2 Ciba Orange R	62.6	25.0	8.34	4.17	39	59	0.43

[a] Ciba Orange R

[b] Free of pyritic sulfur

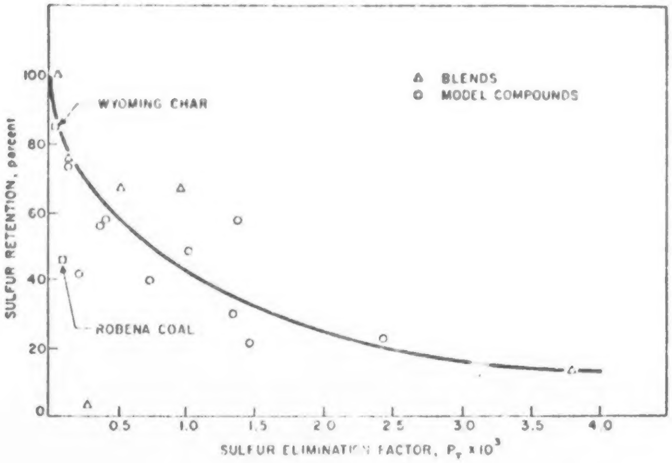


FIGURE 14. SULFUR ELIMINATION DURING PYROLYSIS OF MODEL SULFUR COMPOUNDS (81)

It is generally thought that much more ammonia is produced than is shown above and that ammonia undergoes further decomposition at the conditions in the oven. The temperature of formation of ammonia is not the same for all coals; with some, ammonia formation begins at a temperature as low as 300 C, but with others it begins at temperatures in the range 400 to 500 C.(80) The factors favoring ammonia formation from coal were not defined in literature. There has been speculation by researchers in the field that the mineral or ash content of coal may be important to ammonia yields.(80)

Metal Contaminants.(82) In a by-product coking plant processing 2000 tons of coal per day, it was shown that the bulk of the ash is recovered from the bottom of the coking oven. The elements that showed a marked decrease were gallium, germanium, nickel, lead, tin, vanadium, and zinc. The feed to the ammonium plant contained high concentrations (1.93 percent) of germanium. The ash from the ammonium sulfate liquor contained 10 percent nickel. The tar ash was higher than the coal ash in silver, arsenic, bismuth, cadmium, copper, gallium, germanium, nickel, lead, antimony, tin, and zinc. The ash collected in the mains between the by-product oven and the gas holder had the same metal contaminant distribution as in the ash at the bottom of the ovens. The condensate collected at the suction of the first-stage compressor consisted of alkalies, silicon, silver, arsenic, copper, gallium, germanium, molybdenum, phosphorus, lead, antimony, tin, and zinc. Silver, arsenic, gallium, lead antimony, tin, and zinc were concentrated from 15 to more than 100 times the levels found in the original ash.

Producer gas units show inorganic-element enrichment similar to that given for coke-oven and water-gas units.(82)

2.2.3 Removal of Sulfur and Nitrogen Contaminants

The extent of sulfur and nitrogen removal achieved by the influence of many reagents is discussed below and is almost exclusive for each coal. Coals by nature are heterogeneous, such that two coals of similar rank may not give similar contaminant removal by carbonization under identical treatments. For example, the desulfurization of coke has at times been influenced by the ratio of the types of sulfur in the coal. Thus, numerous and often conflicting reports on the effectiveness of various reagents on contaminant removal have been published. In the following pages a brief description is given of the sulfur and nitrogen removal during the pyrolysis or carbonization of coal as influenced by the presence of gases, acids and alkalies, and of high temperatures.

Influence of Gases. In a study completed in 1932,(90) it was shown that sulfur in coal was converted to volatile sulfur compounds during carbonization. Sulfur elimination at 1000 C was 50 to 60 percent with N_2, CO_2, CO, CH_4, and C_2H_4; 81 percent with NH_3; 87 percent with H_2; and 76 percent with water gas. At 800 C, steam gave 84 percent removal and water gas with HCl gave 72.5 percent removal. Partial removal of pyrite by oxidation and leaching followed by carbonization in H_2 gave 93 percent sulfur removal. Instantaneous carbonization in H_2 removed 59 percent of the sulfur.(90)

Studies were made to determine the conditions of carbonization that would produce a coke of minimum sulfur content.(91,92) The effects of passing ammonia gas over the coal during heating and of inorganic compounds, e.g., aluminum oxide and iron oxide, that would decompose ammonia were studied. The desulfurization actions of hydrogen and of nitrogen at 800 C, when added at virtually double the rate equivalent to the hydrogen and nitrogen in ammonia were much less effective than when only ammonia was used. The decomposition of ammonia produced "nascent" hydrogen. The relative proportion of organic to inorganic sulfur in coal influenced the distribution of sulfur in the coal gas, as shown in Table 28 (coal treated at 800 C with ammonia) but Ledo coal with the higher organic sulfur produced a coal gas with 68 percent H_2S compared with 45.6 percent for Pittsburgh coal.

TABLE 28. INFLUENCE OF ORGANIC AND INORGANIC SULFUR IN COAL AND ITS REMOVAL BY H_2 AND NH_3 DURING CARBONIZATION (91)

Coal	Sulfur Coal, percent			Coal Sulfur in Gas, %
	Organic	Pyritic	Sulfate	
Illinois No. 6 (No. 6 mine, Saline Co.)	1.30	2.12	0.13	53.2 46.7*
Pittsburgh (Shannopin mine)	1.08	1.15	0.18	45.6 39.4*
Ledo (high-volatile A-bituminous), Assam-India	7.13	0.32	0.09	68.1 59.5*

* Without NH_3.

The amount of ammonia decomposed was found to correlate directly with the sulfur removal from the coal. In the case of a low-ash coal (1.7 percent), e.g., Ledo, the addition of inorganic compounds that decomposed the ammonia was found to be helpful.

The effectiveness of CO, steam, H_2, and water gas (N_2, CO, H_2) in removing sulfur from coal as H_2S during the carbonization increases in the order mentioned.(93) The results are different from those reported by Snow,(90) probably on account of the difference in the type of coal used.

In desulfurization of coke with air, at 500 C, a large part of the FeS_2 was converted to Fe_2O_3 and sulfur, without appreciable oxidation of the coke itself. The free sulfur formed from the above oxidation was retained in the coke in an adsorbed form and could not be removed by vacuum treatment at 500 C or by increasing the temperature to 650 C. Alternate, repeated roasting and vacuum treatment increased the elimination of free sulfur.(94)

In another study,(94) it was found that the nature of the coal used affected the hydrogen sulfide yield more than the ammonia yield, because of the sulfur combined with inorganic elements such as iron and calcium. On heating the coke in nitrogen, very little hydrogen sulfide was evolved up to 1000 C and very little sulfur was lost from the coke. On heating in hydrogen, hydrogen sulfide evolved steadily up to 800 C and then decreased. At 900 C the evolution started again. When the treatment was ceased at 1000 C, 93.8 percent of the sulfur in the coke had been removed as hydrogen sulfide. No effect corresponding to the dissociation of ammonia was noticed. On heating with steam, the loss of sulfur was rapid but not more so than with hydrogen up to 800 C. With hydrogen and steam, the sulfur in coke was attacked at 800 C, at which temperature the nitrogen compounds were little affected.(95) In yet another study the treatment of coke with steam at 450 to 550 C produced H_2S and desulfurized the coal bed.(96)

In a fluidized bed devolatilization study, substantial desulfurization of coal was observed with steam during the devolatilization process. The sulfur removal was 76 percent at 600 C while only 38.5 percent at 800 C.(9 A study showed that the sulfur content of the coke was reduced to a greater degree by cooling the coke in a hydrogen atmosphere than by coking in the hydrogen and that wet hydrogen was effective in decreasing sulfur from 7.43 percent to 3.65 percent.(98) Similarly, the treatment of coke after carbonization with the moist-air gave only a slight reduction in sulfur. But the use of coal gas, CO_2-free coal gas, and CO during carbonization reduced the coke sulfur from 4.7 to 3.1 percent; in the presence of water vapor, coke containing 2.75 percent sulfur was produced. The most effective treatment was provided by intermittent blasts of oil gas and steam to yield a coke containing 0.79 percent sulfur.(99)

For the sake of completeness, the following brief descriptions of the influence of gases during carbonization on sulfur and nitrogen removal are presented.

It has been reported that the treatment of Hungarian coals with ammonia removed the organically bound sulfur.(100) As mentioned earlier, this method could be selective for Hungarian coals.

Char obtained after carbonization of coal at 427 to 760 C was desulfurized at 593 to 927 C in the presence of hydrogen and methane at a pressure of at least 5 atm for a period of 10 to 100 minutes. The gas contained 5 volume percent methane. A reduction in sulfur content of 50 percent or greater was obtained.(101) In another study, it was reported that coke with lower than normal sulfur contents could be prepared by carbonization in a stream of ammonia or a stream of coke-oven gas. Coke-oven gas was considered more economical.(102)

It was reported that desulfurization of coke by treatment with water and air during the quenching process must be started at relatively high temperature. If it is started at 800 C with moist air and continued below 400 C with water, the sulfur content could be reduced from between 1.7 and 2.5 percent to between 0.26 and 0.5 percent in 6 to 9 minutes, with an oxidation not exceeding 1 to 2 percent of the coke.(103) In another method, a steam-air mixture at 350 C decreased the sulfur content by 60 to 80 percent.(103) In contrast, the use of superheated steam at 400 to 800 C to desulfurize coke would remove only 10 percent of the sulfur content of the coke.(104) On the other hand, steam with hydrogen is found to be more effective for the desulfurization of coke than hydrogen alone.(105)

Chlorine gave best results for desulfurization as compared with coke gas and steam and included the study of the additions of NaCl, $CaCO_3$, CaO, $MgCO_3$, MgO, and iron ore during coking.(106,107) In other approaches, the sulfur content of coke was lowered by introducing Cl_2 or HCl into the coking chambers, and the chlorination of coke at 500 to 1000 C removed all the sulfur present as sulfide, but not the organic sulfur.(108) When coke was treated with hot chlorine or chlorinated organic vapors at the close of the coking operation, soluble salts could be removed by washing.(109)

Influence of Added Alkalies and Acids. In an extensive study completed in 1943, the effects of acids and alkalies upon carbonization products of coal were investigated.(110) The treatment with nitric acid produced some nitration but direct oxidation also occurred. With sulfuric acid there was limited oxidation and some fixation of the sulfur in the residue. The sulfur content of the semicoke increased with the period of time of sulfuric acid treatment for all coals. Treatment of coal with 10 percent sodium hydroxide eliminated most of the fixed nitrogen in noncaking coals but none in caking coals. Similar treatment with calcium hydroxide showed a tendency toward fixation of nitrogen in the coke--over 90 percent in noncaking coal. Carbonization of coal treated with 2.01 percent lime showed a reduction in sulfur content in the gas (20.48 grains versus 36 grains per 100 ft^3), and the yield of cyanogen (C_2N_2) doubled. It was found that organic sulfur in the gas was reduced more by this treatment in horizontal retorts than in vertical retorts, but that hydrogen sulfide increased.(110)

The addition of sodium carbonate or lime to the coal produced a coke with less sulfur as shown in Table 29. Leaching of the treated coke with hydrochloric acid produced a low-sulfur coke. It is also shown in Table 29 that on carbonization up to 62 percent of the total sulfur is found in the tar and gas.(91,92)

In another study(111) when coal was heated at 800 C in coal gas, the sulfur was reduced from 4.57 percent in the coal to 1.97 percent in the coke. In the presence of 5 percent SiO_2, sulfur was reduced to 1.51 percent, but sodium silicate gave poorer results. Calcium oxide gave a maximum desulfurization of 54 percent, while a mixture of magnesium chloride and calcium oxide (3:1) reduced the sulfur to a minimum of 1.69 percent. With hydrated aluminum oxide, sulfur was reduced to 1.41 percent.(111)

The pretreatment of the coal with saturated solutions of chemicals and then carbonization permitted the removal of the bulk of the sulfur, the amount of removal being 62, 77, 81, and 83 to 92 or 56 to 57 percent, depending on whether the pretreatment agent was NaCl, $MgCl_2$, $ZnCl_2$, $SnCl_2$, or $NaHCO_3$,

TABLE 29. EFFECT OF ADDED CARBONATES AND LIME ON SULFUR REMOVAL AT 800 C FROM ILLINOIS NO. 6 AND LEDO COAL(91)

Test conditions: heating-up period to 800 C, 1.75 hr; carbonization at 800 C, 4.25 hr; 15-g coal sample; through 20- on 35-mesh Tyler series sieves.

Test	Source of Coal	Total Sulfur, %	Added Compound, %	Coke Obtained		Coal Sulfur, %			Total Sulfur Found, %
				Gram	Sulfur, %	In Coke	In Leachings	In Tar and Gas[a]	
23	Ledo	7.47	None	8.45	5.37	40.5	--	50.5	100
22	Ledo	7.47	Na_2CO_3 10	8.39[b]	2.48	18.6[b]	18.1	61.9	98.6
19[c]	Illinois	3.55	None	10.03	2.83	53.3	--	43.0	96.3
21	Illinois	3.55	Na_2CO_3, 10	10.20[b]	2.11	40.4[b]	24.2	32.5	97.1
20	Illinois	3.55	$NaHCO_3$, 10	9.82[b]	2.13	39.3[b]	24.4	34.9	98.6
56	Ledo	7.47	CaO, 10	9.56	5.20	44.4	--	--	98.6
57	Ledo	7.47	CaO, 2	8.71	4.70[d] 4.55[e]	36.5[d] 35.4[e]	--	--	--

(a) Calculated from data in Table II, Reference 91.
(b) Leached coke.
(c) Same as test Q in earlier paper.(1)
(d) Coke washed with boiling water.
(e) Coke washed with hot dilute hydrochloric acid and boiling water.

respectively. Pretreatment with steam and air or steam and ammonia permitted removal of 56 to 58 and 79 to 88 percent, respectively.(112) The addition of NaCl, MgO, or iron ore to the coke did not improve the removal of sulfur by coke gas at 800 C. Increasing the temperature to 1000 C did not help, unless the gas velocity was increased from 30 cc/min to 75 cc/min. The results varied for different cokes and the addition of NaCl prior to carbonization removed more sulfur than the addition of magnesium or calcium carbonates.(113) Another source reports that refluxing coal-tar coke containing 0.9 percent sulfur with bromine for 24 hours removed 4 to 5 percent sulfur and when the same coke was heated at 1000 C with 5 parts by weight of copper powder (with exclusion of air), about 6 to 10 percent sulfur was removed.(114)

The addition of portland cement as 1 to 10 percent of coal during carbonization had no influence on the sulfur present in the coke as sulfate or the organic sulfur and increased the total sulfur of the coke when the carbonization was done at slow rates.(115) This is probably due to the retention of sulfur by the cement while volatile hydrocarbons were lost. In a study in which catalytic amounts of additives were used, it was shown that when less than 0.1 percent chromium oxide and manganese chloride were added to coal, the sulfur content of coke was lower than when they were not present. The sulfide sulfur was removed, and when much organic sulfur was present, the effect of the catalyst on the sulfide sulfur was less. High coking temperatures hindered the action of the catalyst and it was recommended that the temperature should not exceed 900 C.(116)

The effects of addition of dolomite and the sulfur distribution during carbonization are mentioned in a work completed in 1932.(117) Dolomite was added in amounts equalling 10 percent of the charge. The carbonization was carried out at 900 C in a Kropp-Steel retort and the sulfur was retained in the ash.

Influence of High Temperatures, Novel Processes, and Heating Rates. Flash irradiation (rapid heating of fine coal particles by exposure to pulses of high intensity energy source such as a laser beam) of coal produced some products similar to those in high-temperature carbonization but gave high yields of hydrogen cyanide, acetylene, and carbon monoxide. Temperatures as high as 2000 C were obtained.(118)

A novel process for calcining fluid coke particles in order to desulfurize is carried out in a fluidized bed superimposed directly on a moving bed of fluid coke. The sulfur content is reduced from 6 percent to 2 percent.(119)

In the accounts of studies completed prior to 1935, several researchers reported on the removal of sulfur during carbonization. From the experimental study by Woolhouse(120), it was concluded that:

(1) The pyrites began to decompose between 300 and 400 C with the formation of ferrous sulfide. The decomposition was a maximum between 500 and 550 C and was complete at 550 C. The elimination of sulfur as hydrogen sulfide was a low-temperature phenomenon.

(2) The reducing action of hydrogen evolved during the higher temperatures of carbonization was negligible and complex sulfides were formed.

(3) Hydrogen sulfide is also produced from the decomposition of organic-sulfur compounds.

The decomposition of pyrites in coal during heating in a nitrogen atmosphere is shown in Table 30. The retention of sulfur by the coke was attributed to the thermal stability of ferrous sulfide and the complex carbon-sulfur compounds formed during heating.

TABLE 30. FORMATION OF HYDROGEN SULFIDE DURING THERMAL DECOMPOSITION OF PYRITES (NITROGEN ATMOSPHERE) IN COAL(120)

Temp, C	H_2S as Grams Sulfur During Heating(a)
300-500	--
550	Trace
600	0.007
650	0.008

(a) Pyrite sample weight 0.5 g.

Other conclusions that were made in a study completed by Powell(121) in 1920 were as follows.

(1) Decomposition of pyrite to ferrous sulfide is complete at 500 C

(2) Reduction of sulfates to sulfides is complete at 500 C

(3) Formation of hydrogen sulfide from part of organic sulfur (25 to 30 percent) is most active below 500 C

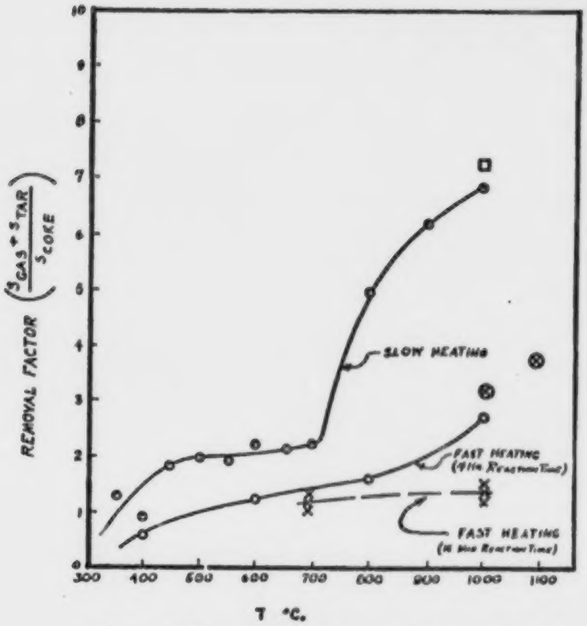
(4) Decomposition of a small part of organic sulfur takes place forming volatile sulfur compounds with carbon

(5) Decomposition of a portion of the ferrous sulfide takes place, yielding sulfur which in turn combines with carbon.

In a study of the desulfurization of brown coal from New Zealand, it was shown that during carbonization hydrogen sulfide was formed below 600 C and up to 70 percent of the sulfur was removed.(122) Another study published in 1924 investigated the mechanism of sulfur removal.(123) Two coals, one in which pyrite was absent and one in which a small amount was present, were carbonized. The evolved gases at 560 C from the coal without pyrite contained little hydrogen. This indicated that removal of organic sulfur did not depend wholly on the action of hydrogen. Most of the hydrogen sulfide was evolved below 560 C from the coal in which pyrite was present. Experiments to determine the effect of the heating rate to 560 C indicated that all the hydrogen sulfide produced during coking did not escape but instead was partially decomposed. The addition of anthracite to the coals caused a greater elimination of sulfur from coke.(123)

Influence of Kinetics. The removal of sulfur by heating coal in hydrogen shows that the desulfurization reactions on coal pyrolysis and gasification are inefficient under equilibrium conditions. Sulfur removal from coal in terms of a removal factor and heating time and the activation energies involved in sulfur removal reactions are shown in Figure 15.(124-126) Experimental studies that provide kinetic data on the removal of sulfur are essential to the development of processes for the removal of sulfur from coal.

Gorin et al.(126) in their study of coal desulfurization with dolomite in the CO_2 Acceptor Process, observed "total inhibition isotherms" and from their data concluded that "the net rate of desulfurization is determined by the competition between two processes--(1) thermal fixation of the sulfur to produce a more stable form and (2) rate of removal by hydrogen while in the labile form". It was suggested that several independent reactions produced hydrogen sulfide during the heating of coal in hydrogen, that at low



Sulfur removal factors for coal pyrolysis in hydrogen at one atmosphere.

●, ○ R. D. Snow, Ind. Eng. Chem. 24, 903 (1932).

X fast heating; 15 minute reaction time

⊗ fast heating; 4 hour reaction time

□ slow heating (33° /min)

Reaction	E(kcal/mole)	k_0	
(1) $(Org\text{-}S)_I + H_2 \longrightarrow H_2S$	34.5	3.1×10^{10}	(1)
(2) $(Org\text{-}S)_{II} + H_2 \longrightarrow H_2S$	41.5	2.8×10^{11}	(1)
(3) $FeS_2 + H_2 \longrightarrow H_2S + FeS$	47	2.8×10^{13}	(1)
(4) $FeS + H_2 \longrightarrow H_2S + Fe$	53	2.1×10^{13}	(1)
(5) $(C\text{-}S)_{III} + H_2 \longrightarrow H_2S_{ads}$	32	2.3×10^{6}	(1)
(6) $H_2S^{(I)}_{ads} \longrightarrow H_2S_{gas}$	10	50	(3)
(7) $H_2S^{(II)}_{ads} \longrightarrow H_2S_{gas}$	43	2.4×10^{9}	(3)
(8) $Fe + H_2S \longrightarrow H_2 + FeS$	18	6.5×10^{6}	(2)
(9) $(C) + H_2S \longrightarrow H_2S_{ads}$	32	2.3×10^{5}	(2)
(10) $CaO + H_2S \longrightarrow H_2O + CaS$	38	4.7×10^{13}	(2)
(11) $CaCO_3 \longrightarrow CO_2 + CaO$	58	3.8×10^{15}	(3)

(1) Units of $(\text{atm. } H_2)^{-1}\ \text{min}^{-1}$

(2) Units of $(\text{atm. } H_2S)^{-1}\ \text{min}^{-1}$

(3) Units of min^{-1}

FIGURE 15. SULFUR REMOVAL DURING COAL PYROLYSIS IN HYDROGEN STREAM AND REACTIONS PRODUCING H_2S DURING PYROLYSIS(124,126)

temperatures some of the organic sulfur was converted to H_2S, and that the rate at which the sulfate was converted to sulfide with the evolution of H_2S by reaction with hydrogen was quite slow. The overall reaction of hydrogen with organic sulfur involved two steps:

$$(1) \quad H_2 + (C - S)_{organic} \longrightarrow H_2S_{(adsorbed)}$$

$$(2) \quad H_2S_{(adsorbed)} \longrightarrow H_2S_{(gas)} \quad .$$

Reaction (1) is rate determining at low temperatures and Reaction (2) is rate determining at high temperatures.(124)

2.3 Contaminant Removal Via Coal Liquefaction

A combination of the use of heat, solvents and hydrogen pressure has been successfully employed for liquefying coal to produce liquid and more recently solid fuels. Small increases in the H/C atomic ratio of that present in coal produces a liquid which at ambient temperatures is a solid fuel. Larger increases in the H/C ratio, which requires higher hydrogen pressures and catalysts will produce liquid fuels. Although other approaches for the formation of liquid products from coal have been attempted (e.g. pyrolysis), the concept of liquefaction through hydrogenation and its effect upon sulfur and nitrogen impurities have been studied extensively.

In this section a summary of coal liquefaction processes is given with specific emphasis on the catalysts employed and how the sulfur and nitrogen impurities are effected during the conversion of solid to a liquid fuel. In addition detailed consideration is given to the mechanisms by which the sulfur and nitrogen impurities are acted upon during hydrogenation of the coal or primary coal liquid. The fate of the mineral matter and related trace elements associated with coal upon liquefaction is also discussed.

2.3.1 Catalysts

The addition of hydrogen to coal does not occur readily and catalysts have been used extensively to maintain practical process conditions and also to increase the reactor throughput. Catalysts form an important criteria for evaluating the liquefaction and subsequent sulfur and nitrogen contaminant-removal capabilities of a process. Innumerable catalysts and their combinations have been investigated in coal liquefaction. Some of the successful catalysts used in the German plants and also at the British and Bureau of Mines pilot plants are discussed in Table 31. The saturation catalysts in this table promoted hydrogenation and the splitting catalysts promoted the production of lighter oil fractions. The proven heterogeneous catalysts essentially consist of one of the following active components: cobalt-molybdenum oxides, nickel-tungsten sulfide, or tungsten sulfide. The cobalt-molybdenum oxide catalyst is the choice of the presently developing processes, e.g., Synthoil, H-Coal.(130) Such catalysts operate under vigorous conditions, e.g., hydrogen pressure of 1000 to 4000 psig, temperatures of 350 to 500 C, high turbulence around the fixed-bed catalyst or as a moving bed, residence time of minutes or more, and in the presence of sulfur, nitrogen, and coal ash (including trace elements) contaminants. The catalysts are deactivated by chemical combination with or adsorption of sulfur and nitrogen contaminants. The catalysts are also deactivated by the heavy tar and trace-elements physically deposited on them.

2.3.2 Liquefaction Processes and Sulfur and Nitrogen Removal

Significant coal-liquefaction processes with their contaminant-removal capabilities are briefly discussed in Table 32. In these processes the sulfur and nitrogen of the coal are removed as H_2S and NH_3. The process scheme at the Blechhammer installation, a typical German liquefaction plant, is shown in Figure 16. The material balances are also shown in this figure. The first-stage hydrogenation occurred in the liquid phase vessel (stall in figure), and the middle oil obtained from the distillation product was further hydrogenated in the saturation vessel. The splitting vessel which functioned as the last stage of the process, produced refined aviation gasoline. It was at this stage that a sulfur-free product was obtained. The data on the sulfur balance from such coal-conversion plants are shown in Table 33. At the Blechhammer plant, where coal was hydrogenated using sulfide/sulfate catalysts, as much as 47 percent

TABLE 31. CATALYSTS FOR HYDROGENATION OF COAL COAL-OILS USED PRIOR TO 1950

[Source, Appendix of (127)]

Catalyst number	Composition	Principal functions and use[2]
	I. G. Farben industries A. G.	
2365	A mixture of $MoO_3 \cdot H_2O$, ZnO, and MgO	Used in early I. G. Farben single-stage process.
3510	53.5 percent MoO_3, 30 percent ZnO, and 16.5 percent MgO.	Saturation, refining,[3] and aromatization; used in early I. G. Farben single-stage process and aromatization process.
3884	75 percent MoO_3, 8 percent CrO_3, 16.5 percent kaolin, and 0.5 percent Al powder.	Used in early I. G. Farben single-stage process.
5058	100 percent WS_2	Saturation, refining,[3] and splitting; used in early I. G. Farben single-stage process and in the saturation stage of I. G. Farben two-stage process.
5615	See catalyst 6718	
6434	10 percent WS_2 and 90 percent HF-treated fuller's earth.	Splitting, possibly also saturation and aromatization; used in the splitting stage of I. G. Farben two-stage process.
6525	10 percent WS_2 and 90 percent FeS	Phenol reduction, saturation, and aromatization; used in aromatization process.
6561	2 percent WS_2, 18 percent FeS, and 80 percent active char.[4].	Do.
[1]6718	85 percent WS_2 and 15 percent NiS. (Also called 5615).	Saturation, refining,[3] and dehydrogenation.
6719	22 percent WS_2, 3 percent NiS, and 75 percent FeS.	Saturation.
7019	15 percent Cr_2O_3, 5 percent V_2O_5, and 80 percent active char.[4]	Aromatization; used in aromatization process.
7846	10 percent MoO_3, 3 percent Ni_2O_3, and 87 percent Al_2O_3.	Saturation and refining;[3] used in the saturation stage of I. G. Farben two-stage process.
7846-W-250	See catalyst 8376	
7935	15 percent MoO_3 and 85 percent Al_2O_3	Refining;[3] used in the DHD process.
8376	27 percent WO_3, 3 percent Ni_2O_3, and 70 percent Al_2O_3. (Also called 7846-W-250).	Saturation and refining;[3] used in the saturation stage of I. G. Farben two-stage process.
	Ruhröl GmbH	
K413	0.4 part Mo (as sulfide), 2 parts Cr (as oxide), 5 parts ZnO, 5 parts elemental sulfur, and 100 parts fuller's earth.	Used in the single-stage Welheim process.
K534	0.6 part Mo (as sulfide), 2 parts Cr (as oxide), 5 parts ZnO, 5 parts elemental sulfur, 100 part fuller's earth.	Do. USBM. Louisiana Mo.
K535	0.7 part Mo (as sulfide), 2 parts Cr (as oxide), 5 parts ZnO, 10 parts elemental sulfur, and 100 parts fuller's earth.	Do.
K536	0.7 part Mo (as sulfide), 2 parts Cr (as oxide), 5 parts ZnO, 5 parts elemental sulfur, and 100 parts fuller's earth.[5]	Do.
	Imperial Chemical Industries, Ltd. (Billingham)	
231	20 percent FeF_3 and 80 percent fuller's earth	Splitting; used in the splitting stage of I. G. Farben two-stage process.

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[1] Based on: Badische Anilin und Soda Fabrik, A. G. High Pressure Hydrogenation at Ludwigshafen-Heidelberg, v. 1A, General Section, Fiat Final Rept. 1317. Trans. by W. M. Sternberg, Central Air Document Office, Dayton, Ohio, 1951, 183 pp. PB120607.

[2] All catalysts for vapor-phase hydrogenation can be used in the TTH process which is a mixed-phase process consisting of both vapor and liquid phases.

[3] Removal of oxygen, nitrogen, and sulfur compounds.

[4] Low-temperature char.

[5] Commercial sample differed slightly from this composition. See Bureau of Mines' analysis in table 31 and in the section on preparation of K catalysts, chapter 3.

TABLE 32. SIGNIFICANT COAL-LIQUEFACTION PROCESSES PAST AND PRESENT

Process	Status	Description/Operating Conditions	Contaminant Removal
Bergius (127,128,133)	Plant in operation prior to 1944 (Germany)	Primary hydrogenation. Fine ground coal mixed with a process-derived liquid and a catalyst. Catalyst, Iron oxide, Luxmasse. Pressure 3000 - 10,000 psig, temperature 482 C.	H_2S, NH_3 formed. Ash minerals removed by fuel filtration.
TTH Process (127,128) (Tief Temperatur Hydrierung)	Plant in operation prior to 1944. (Zeitz, Germany)	Hydrogenation of low temperature tar to gasoline. Fixed-bed catalyst, tungsten sulfides. Pressure 4500 psig, temperature 360-390 C.	H_2S, NH_3 formed.
I. G. Farben (127)	Leuna Commercial plant began operation in 1927.	Liquid-phase hydrogenation of Brown Coal (German). Initially no catalyst later molybdenum and then iron salts. Leuna used a 5.9 percent sulfur coal.	Sulfur-free liquids produced. Sulfur balances shown on an later table.
Welheim Process (127)	Plant in operation prior to 1944.	Coal-derived-oil hydrogenated in the vapor phase. Catalysts, K-series shown in Table 87. Pressure 10,000 psig, temperature 480-502 C.	Temperature and pressure high enough to remove all sulfur and nitrogen (postulate).
Coal Hydrogenation (129)	Carbide & Carbon Chemicals Co. plant placed on stream in 1952. 300 tons/day	Coal hydrogenation, dried 20 mesh coal; prepare coal oil slurry. Pressure 4000-6000 psig, temperature 449-538 C.	Some sulfur and nitrogen removed as H_2S and NH_3. Product streams consist of quinolines, anilines.
Catalytic Coal (130) Liquefaction (CCL)	January, 1975, 1 ton/day pilot plant at Harmarville began operation.	Coal dried and pulverized, mixed with process oil and the slurry forced over a fixed-bed catalyst. Highest conversion for high-ash coals. Pressure 2000 psig, temperature 480 C.	Gulf claims process produces low sulfur and nitrogen products.

TABLE 32. (Continued)

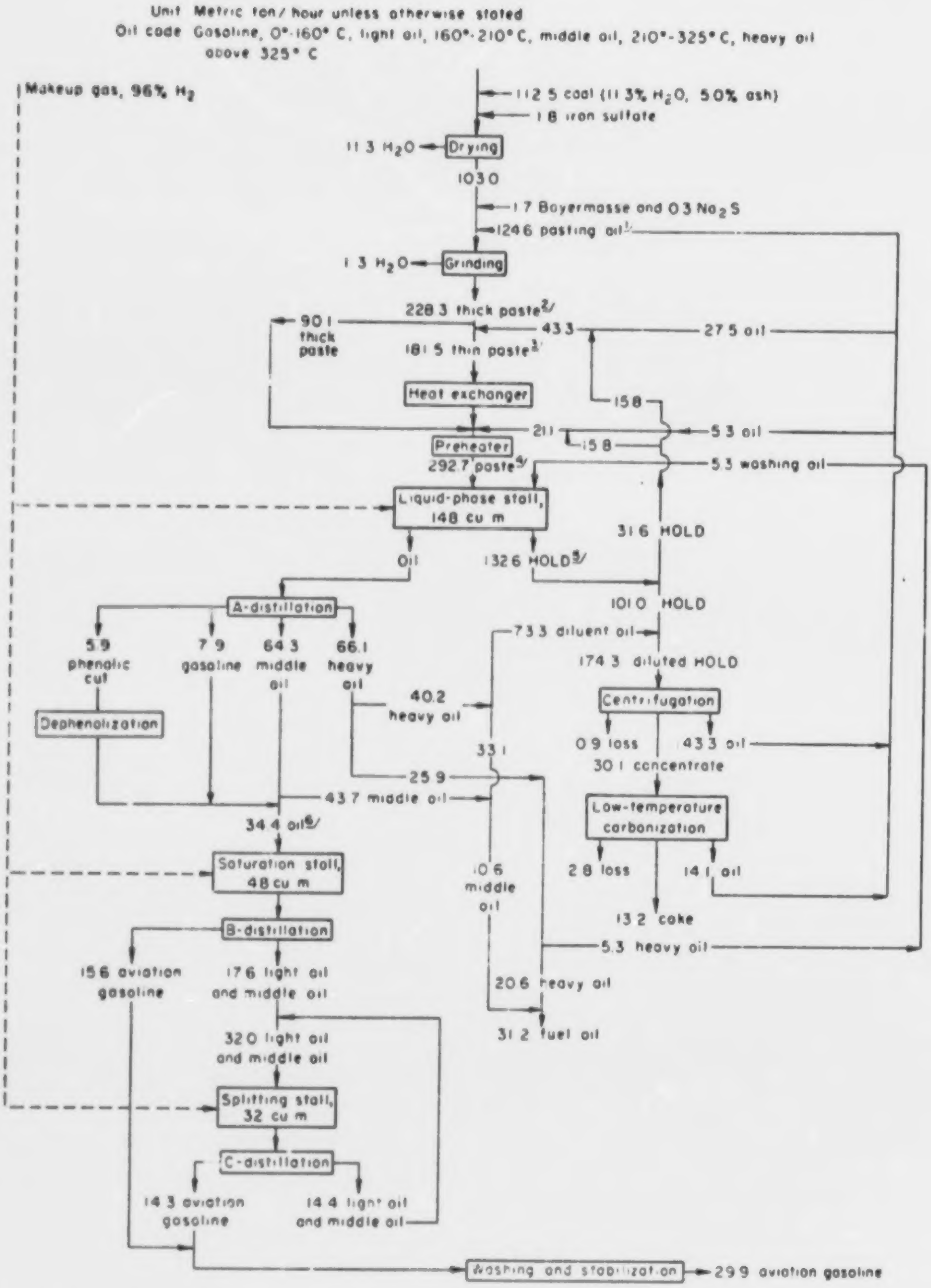
Process	Status	Description/Operating Conditions	Contaminant Removal
Coal-Oil-Gas Refinery (COG)(130)	(1) Pittsburgh and Midway Mining Co. (Gulf Oil) (S.R.C.) (2) Bituminous Coal Research (Bi-Gas) Costing for a 10,000 TPD demonstration plant in progress by Ralph M. Parsons.	(1) Coal liquefaction by the solvent refining of coal (S.R.C.); temperature 454 C, pressure 1000 psig (2) Wet filter cake from liquefaction gasified, Bi-Gas; temperature 1649 C, 200 psig.	During liquefaction some sulfur goes to H_2S. Asphaltene type material containing sulfur, nitrogen, and trace elements is gasified.
Consol Synthetic Fuel (CSF) (Project Gasoline)(130)	Consolidated Coal Company A 20 TPD plant completed in 1967. In 1974 plant facilities to be altered to produce fuel oil (Cresap, W. Va.).	Coal crushed and dried is preheated in a fluidized bed to 232 C, then slurried in a coal-derived liquid and extracted at 410 C and 150-400 psig. Solid residue pyrolyzed at 427-482 C. Catalysts used cobalt-moly and zinc chloride.	Complete desulfurization achieved by hydrotreating with $ZnCl_2$.
Costeam(130,131)	U.S. Bureau of Mines. Bench-scale work in progress.	Slurry of coal in coal-derived oil in the presence of CO is heated to 427 C at 4000 psig. Designed for lignites.	Desulfurization not as good as achieved with hydrogen.
Exxon Liquefaction(130)	Exxon. Pilot plants to up to 0.5 TPD; design of 200 TPD pilot plant on the way.	Crushed coal slurried with a recycle solvent, preheated 427 C, pressure 2000 psig of hydrogen. Products distilled. Quality of final products improved by hydrogenation.	Desulfurization of liquid products carried out in the hydrogenation step.

TABLE 32. (Continued)

Process	Status	Description/Operating Conditions	Contaminant Removal
Gas Extraction(130)	National Coal Board, England.	Pulverized coal treated with compressed gases at 177-204 C causing a portion of coal to solubilize. Advantages over liquid extraction of coal: (1) no filtering necessary to remove insoluble residue, (2) recovery of gaseous solvent is complete, (3) extract is porous, (4) more mobile liquids than in solvent extraction of coal.	The temperature of treatment is low to produce any desulfurization via the pyrite or organic sulfur. (Postulate
H-Coal(130,132)	Developed by Hydrocarbon Research. Process Unit 3 TPD.	Coal slurried with coal derived liquid and feed to the base of a cobalt/moly ebullating bed reactor. Pressure 2250 to 2700 psig, temperature 454 C.	Ill. No. 6 coal, 5 percent sulfur, 1 percent nitrogen produces a fuel oil with 0.43 percent sulfur and 1.05 percent nitrogen.
Intermediate Hydrogenation(130)	University of Utah Bench scale.	Stannous- or zinc chloride-impregnated coal hydrogenated at 499-549 C at 2000-2500 psig.	High levels of desulfurization should occur due to the fine particle size, the catalyst, and temperatures.
Synthoil(130,132-134)	U.S. Bureau of Mines Design of 10 TPD in progress.	Pulverized, dried coal slurried in coal liquid and with hydrogen passed over cobalt-moly catalyst at 454 C and 2000-4000 psig.	Kentucky coal 5.5 percent sulfur, 1.2 percent nitrogen produces a product with 0.2 to 0.7 sulfur.
SRC (PAMCO)(130) (Solvent Refined Coal)	Pittsburgh Midway Coal Co. Ft. Lewis, Wa. Plant capacity 50 TPD.	Dissolves coal as in the process developed by A. Pott and H. Broche in Germany in the 1920's.	Demineralized, low sulfur extract from coal.
SRC(135,136)	Electric Power Research Institute, Southern Services Plant capacity 6 TPD.	Dissolves coal under pressure in the presence of hydrogen.	Ash minerals reduced to 0.1 percent, sulfur content reduced to 0.3 percent.

TABLE 32. (Continued)

Process	Status	Description/Operating Conditions	Contaminant Removal
SRC as feed for liquid fuel process (137)	E. Gorin, U.S. Pat. 3,143,489, Aug. 4, 1964.	**The liquids produced from coal are hydrocracked to remove sulfur, oxygen, and nitrogen.**	Coal contained 4.8 percent sulfur, 1.4 percent nitrogen, and 13 percent ash. First extract contained 1.86 percent sulfur, 1.45 percent nitrogen, +193 C hydrorefiner product; contained <50 ppm sulfur, <10 ppm nitrogen. The coal extract contained 0.15 weight percent ash.
Solvent Extraction in the presence of hydrogen sulfide (137)	J. G. Gatsis, U.S. Pat. 3,503,863, Mar. 31, 1970.	Coal solubilized in coal-derived liquid in the presence of 1-2 percent (of hydrogen present) hydrogen sulfide	Depending on process operating conditions, the sulfur and nitrogen contaminants could be removed.
Deashing in the presence of acids (solvent extracted coal products) (137)	E. Gorin, et al., U.S. Pat. 3,232,861, Feb. 1, 1966.	Deashing of ash-containing coal extracts. Acidic (HCl) aqueous solution is used.	The ash content was lowered from 0.13 to 0.085 and from 0.28 to 0.12 weight percent.
Catalytic Hydrogenation of carbonized coal vapors (137)	R. C. Perry, C. W. Albright, U.S. Pat. 3,281,486, Jan. 25, 1966.	Presence of conventional hydrotreating catalysts prevents condensation of tar to heavy materials.	As heavy condensed products are not formed, the sulfur and nitrogen compounds are low in the product.



Unit Metric ton/hour unless otherwise stated
Oil code Gasoline, 0°-160° C, light oil, 160°-210° C, middle oil, 210°-325° C, heavy oil above 325° C

Makeup gas, 96% H_2
112.5 coal (11.3% H_2O, 5.0% ash)
1.8 iron sulfate
11.3 H_2O
Drying
103.0
1.7 Bayermasse and 0.3 Na_2S
124.6 pasting oil[1]
1.3 H_2O
Grinding
228.3 thick paste[2]
90.1 thick paste
43.3
27.5 oil
181.5 thin paste[3]
Heat exchanger
15.8
21.1
15.8
5.3 oil
Preheater
292.7 paste[4]
5.3 washing oil
Liquid-phase stall, 148 cu m
31.6 HOLD
Oil
132.6 HOLD[5]
101.0 HOLD
A-distillation
73.3 diluent oil
5.9 phenolic cut
7.9 gasoline
64.3 middle oil
66.1 heavy oil
174.3 diluted HOLD
40.2 heavy oil
Centrifugation
Dephenolization
33.1
0.9 loss
43.3 oil
30.1 concentrate
25.9
43.7 middle oil
34.4 oil[6]
Low-temperature carbonization
Saturation stall, 48 cu m
10.6 middle oil
2.8 loss
14.1 oil
13.2 coke
B-distillation
5.3 heavy oil
15.6 aviation gasoline
17.6 light oil and middle oil
20.6 heavy oil
31.2 fuel oil
32.0 light oil and middle oil
Splitting stall, 32 cu m
C-distillation
14.3 aviation gasoline
14.4 light oil and middle oil
Washing and stabilization
29.9 aviation gasoline

1. 45.6 middle oil, 66.5 heavy oil, 12.5 solids
2. 96.2 maf coal, 45.6 middle oil, 66.5 heavy oil, 20.0 ash and organic solids
3. 58.3 maf coal, 41.5 middle oil, 62.6 heavy oil, 19.1 ash and organic solids
4. 96.2 maf coal, 65.2 middle oil, 99.4 heavy oil, 31.9 ash and organic solids
5. 31.9 middle oil, 64.8 heavy oil, 35.9 solids
6. 8.0 gasoline, 5.9 light oil, 20.5 middle oil

FIGURE 16. HYDROGENATION OF BITUMINOUS COAL AT BLECHHAMMER PLANT[127]

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TABLE 33. SULFUR BALANCES FOR HYDROGENATION OF COAL AND TAR IN GERMAN PLANTS(127)

[Metric tons/year unless otherwise stated]

	Scholven, bituminous coal	Gelsenberg, bituminous coal	Pölitz, bituminous coal, pitch, tar, & petroleum residue	Blechhammer, bituminous & brown coal	Leuna, brown coal	Wesseling, brown coal	Brüx, brown coal tar	Böhlen, brown coal tar	Magdeburg, brown coal tar	Zeitz, brown coal tar	Welheim, pitch from high-temperature tar	Lützkendorf, middle oil from bituminous & brown coals
Motor gasoline produced	210,000	300,000	640,000	430,000	530,000	215,000	395,000	200,000	190,000	265,000	125,000	51,000
Feed:												
Quantity	460,000	595,000	868,000	946,000	1,470,000	465,000	500,000	250,000	240,000	320,000	180,000	57,000
Sulfur content, percent of feed	0.73	0.65	0.56	0.63	5.1	0.45	0.39	1.5	1.5	1.5	0.8	0.15
Total sulfur	3,360	3,870	4,860	5,960	75,000	2,090	1,950	3,750	3,600	4,800	1,440	85
Liquid-phase catalyst constituents:												
Ferrous sulfate	—	4,400	5,300	6,750		—	—	—	—	—		
Bayermasse	—	5,800	13,000	8,900	125,000	23,700	—		—	—	—	—
Sodium sulfide	—	1,600	1,300	2,500	—	—	—	—	—	—	—	
Grude coal[1]	—	—		—	—	—	1,500	500	500	—	900	—
Total sulfur	—	1,590	1,700	2,440		—	100	33	33	—	60	—
Sulfur added (as S or H_2S)	1,320	1,900	1,670	1,425	13,500	5,550	4,060	1,200	1,200	—	—	
Water gas for hydrogen production:												
Million cu m	390	800	260	1,160	1,460	600	690	215	215	175	100	43
Sulfur content, percent of gas	0.3	0.3	0.3	0.3	0.6	0.8	0.8	0.8	0.8	0.8	0.3	0.3
Total sulfur	1,550	3,200	1,100	3,480	11,700	6,400	5,500	2,300	2,300	1,850	400	170
Total sulfur input:												
Excluding sulfur in water gas	4,680	7,360	8,230	9,825	88,500	7,640	6,110	4,983	4,883	4,800	1,500	85
Including sulfur in water gas	6,230	10,560	9,330	13,305	100,200	14,040	11,610	7,283	7,133	6,650	1,900	255
Low-temperature coke:												
Quantity	73,000	67,500	124,000	127,000	440,000	76,000	12,000	1,000	1,000	—	5,000	—
Sulfur content, percent of coke	3.15	5.0	4.2	4.9	4.5	6.5	2.28	6.0	6.0	—	3.55	—
Total sulfur	2,300	3,380	5,210	6,200	19,800	4,940	274	60	60	—	177	—
Recoverable sulfur:												
Excluding sulfur in water gas:												
Metric ton/year	2,380	3,980	3,020	3,605	68,700	2,700	5,836	4,923	4,773	4,800	1,323	85
Metric ton/1000 metric tons motor gasoline produced	11.33	13.27	4.72	8.38	129.62	12.56	14.77	24.62	25.12	18.11	10.58	1.67
Including sulfur in water gas:												
Metric ton/year	3,930	7,180	4,120	7,085	80,400	9,100	11,336	7,223	7,073	6,650	1,723	255
Metric ton/1000 metric tons motor gasoline produced	18.71	23.93	6.44	16.48	151.70	42.33	28.70	36.11	37.23	25.09	13.78	5.00

---

[1] Iron catalyst on low-temperature char from brown coal.

of the sulfur was retained in the low-temperature coke and the rest was evolved as hydrogen sulfide such that the motor gasoline produced was sulfur-free as shown in Table 33.

The distribution of sulfur and nitrogen in the products from Bureau of Mines coal-liquefaction studies prior to 1941 is shown in Table 34. In Run 17-1, over 60 percent of the sulfur and nitrogen was found in the heavy oil fractions, while in Run 16-2.40 percent of the sulfur and 56 percent of the nitrogen was found in the heavy fraction. Up to 21 to 26 percent of nitrogen was converted to ammonia, and 35 to 37 percent of sulfur in the feed coal was converted to hydrogen sulfide.

The coal-liquefaction processes presently being developed will produce low-sulfur and possibly low nitrogen fuels (depends on process). Three of these processes are shown in Figure 17. These processes use catalysts to hydrogenate the coal and convert most of the sulfur and nitrogen to hydrogen sulfide and ammonia. The unreacted coal and the ash minerals are separated by different techniques. In the H-Coal process, both distillation and hydrocyclones are used to remove the heavier fractions (rich in ash minerals) from the lighter fuels. The Exxon Process uses distillation and filters to separate the solids. In the Bureau of Mines Synthoil process, centrifugal filters are used to remove the solids from the oils. Separation of ash minerals and other solids by centrifugal filters is a proven technique and was successfully used by the pre-1945 German plants. However, this technique has operational problems.

2.3.3 Mechanism of Hydrodesulfurization (HDS) and Hydrodenitrification (HDN) of Coal Liquids

Many mechanistic and kinetic models of HDS have been proposed. Some of these catalytic concepts related to petroleum HDS are reviewed in Reference (138). Similar mechanisms have been postulated for the HDS reaction occurring during coal liquefaction and hydrogenation of coal liquids. Moreover, catalysts used in coal liquefaction are of similar composition to those used for HDS processes in the petroleum industry. In the case of petroleum, where the nitrogen content is orders of magnitude lower than that for nonpetroleum crudes (e.g., coal liquids, shale oil, and tar sand oils which contain about 1 to 2 percent nitrogen), it may be justi-

TABLE 34. FATE OF SULFUR AND NITROGEN CONTAMINANTS IN COAL LIQUEFACTION STUDIES
Bureau of Mines Pre-1941 (Source, Table 13)(127)

	Run	
	17-1	16-2
Operating Conditions:		
Pressure, atm	200	200
Temperature, C	440	433
Coal in Paste, percent	46.5	47
Hydrogen, vol per vol of reactor per hour	0.63	2.3
Throughput, vol of paste per vol of converter per hour	0.52	0.50
Product:		
Net Oil, percent of maf oil	63	66
Ratio of Overhead to Heavy Oil	0.54	0.62
Mass Balance, percent of input:		
Oxygen:		
H_2O(a)	59.2	47.5
Overhead Oil(b)	15.4	22.6
Heavy Oil	25.4	29.9
Nitrogen:		
NH_3	21.3	25.9
Overhead Oil	16.4	18.5
Heavy Oil	62.3	55.6
Sulfur:		
H_2S	35.0	57.0
Overhead Oil	2.5	2.9
Heavy Oil	62.5	40.1

(a) A small amount of CO_2 is included.

(b) About 10 percent of this oil boiled above 330 C.

H-COAL

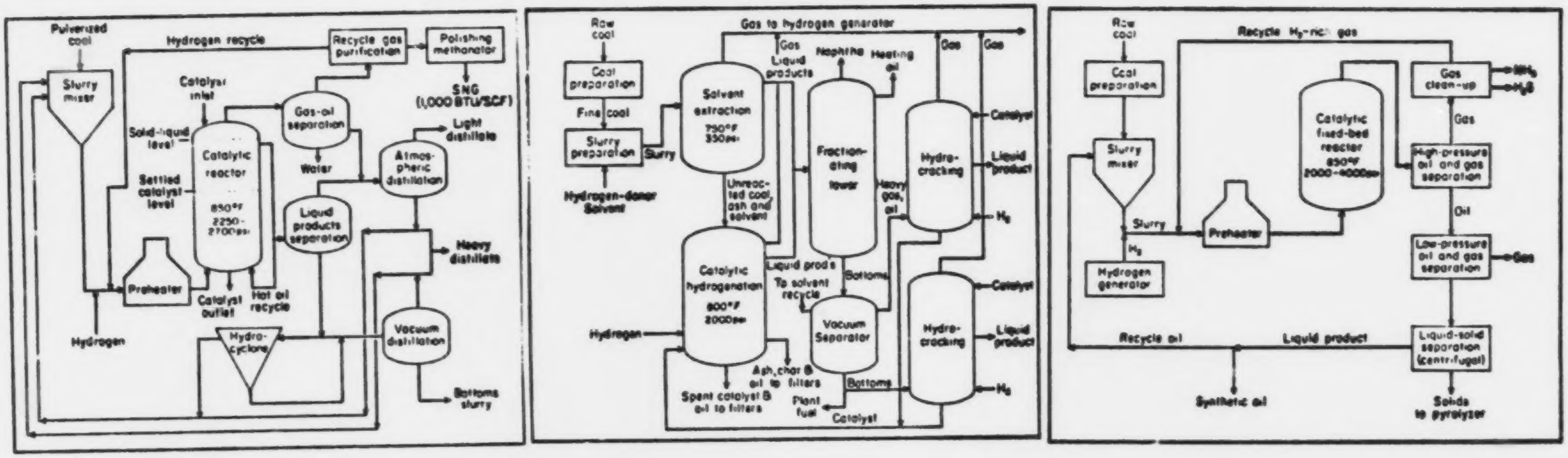
REACTOR	TEMP (°F)	PRESSURE (psi)	REACTANTS	PRODUCTS
CATALYTIC EBULLATED-BED	850	2250-2700	COAL-H_2-OIL	SYNTHETIC CRUDE OIL & GAS

EXXON LIQUEFACTION

REACTOR	TEMP (°F)	PRESSURE (psi)	REACTANTS	PRODUCTS
SOLVENT EXTRACTION	750	350	COAL-H-DONOR SOLVENT	LIQUID PRODUCTS, GAS
CATALYTIC HYDROGENATION	800	2000	COAL-H-DEPLETED SOLVENT-H_2	LIQUID PRODUCTS, REGENERATED SOLVENT, GAS

SYNTHOIL

REACTOR	TEMP (°F)	PRESSURE (psi)	REACTANTS	PRODUCTS
CATALYTIC-FIXED-BED	850	2000-4000	COAL-H_2-OIL	FUEL OIL, GAS



Pulverized coal
Hydrogen recycle
Recycle gas purification
Polishing methanator
SNG (1,000 BTU/SCF)
Slurry mixer
Catalyst inlet
Solid-liquid level
Settled catalyst level
Catalytic reactor
850°F 2250-2700psi
Gas-oil separation
Water
Light distillate
Atmospheric distillation
Liquid products separation
Heavy distillate
Preheater
Catalyst outlet
Hot oil recycle
Hydrogen
Hydro-cyclone
Vacuum distillation
Bottoms slurry
Raw coal
Coal preparation
Fine coal
Slurry preparation
Slurry
Hydrogen-donor Solvent
Gas to hydrogen generator
Gas
Liquid products
Naphtha
Heating oil
Gas
Gas
Solvent extraction 750°F 350psi
Fractionating tower
Hydrocracking
Catalyst
Liquid product
H_2
Unreacted coal, ash and solvent
Heavy gas, oil
Catalytic hydrogenation 800°F 2000psi
Liquid prods
To solvent recycle
Bottoms
Hydrogen
Vacuum Separator
Hydrocracking
Catalyst
Liquid product
H_2
Ash, char & oil to filters
Spent catalyst & oil to filters
Plant fuel
Bottoms
Catalyst
Raw coal
Recycle H_2-rich gas
Coal preparation
Gas clean-up
NH_3
H_2S
Catalytic fixed-bed reactor 850°F 2000-4000psi
Gas
Slurry mixer
High-pressure oil and gas separation
Slurry
Preheater
Oil
H_2
Hydrogen generator
Low-pressure oil and gas separation
Gas
Recycle oil
Liquid product
Liquid-solid separation (centrifugal)
Synthetic oil
Solids to pyrolyzer

FIGURE 17. THREE PROCESSES PRESENTLY BEING DEVELOPED FOR COAL LIQUEFACTION(130)

fiable to investigate mechanisms of HDS and neglect HDN reactions. But for nonpetroleum fuels, such a kinetic and mechanism model would be incomplete using that approach, since both HDS and HDN reactions are interdependent.

Catalysts for HDS and HDN. The catalytic HDS and HDN technology applied to fuels today is based on a few catalysts, e.g., nickel- or cobalt-molybdenum sulfide, nickel sulfide, or nickel-tungsten sulfide catalysts. Catalysts used in the H-Coal or Synthoil liquefaction processes during which HDS and HDN reactions occur, are very similar to the cobalt-molybdenum catalysts used in petroleum HDS and HDN processes. Improvements in these catalysts by way of support material or reactor operation parameters are constantly being reported. The technology to remove sulfur and nitrogen from lighter fractions of fuels, e.g., gasoline or middle distillates, is available. The sulfur and nitrogen removal is accomplished by using catalysts engineered with "dual" capability so that hydrogenation and the HDS and HDN functions are provided by the same catalyst. Coke is periodically burned off the catalyst, which may have a lifetime of several years or more. In the hydrodesulfurization of light feeds, catalyst costs typically account for less than about 10 percent of processing costs, and thus there is no great incentive for developing new catalysts.

It is postulated(139) that for the conventional dual-function catalysts that contain both metallic and acidic sites and are used for the HDS and HDN reactions, a special kinetic site interaction occurs on the catalyst. The role of the metal is to prevent irreversible adsorption of coke and coke precursors on the acidic sites. The metal site is also considered as a source of partially hydrogenated hydrocarbons that are capable of reacting with strongly adsorbed hydrogen-deficient hydrocarbons on the acidic sites(139).

The strongly adsorbed basic organic nitrogen compounds inhibit the hydrogenation of the aromatics as long as they are present on the catalyst. When these nitrogen compounds are transformed to less strongly adsorbed species, such as NH_3, the hydrogenation rate of the hydrocarbons may increase dramatically.

Mechanism of HDS and HDN Processes. The HDS and HDN processes involve a heterogeneous catalyst system. Thus, for contaminant removal, a critical step is the adsorption of sulfur or nitrogen compounds on the active catalyst sites. The adsorbed species may go through splitting reactions, where C-H, C-S, and C-N bonds are broken and/or the adsorbed hydrogen reacts to form species that desorb from the catalyst site. When hydrogenation does not occur, the olefins created on catalyst sites react with themselves to form condensed products. These end up as coke on the catalyst and contain high concentrations of sulfur, nitrogen and metals.

The data for rates of thiophene disappearance and butane formation have been correlated with Langmuir-Hinshelwood-type rate equations as follows.(138)

$$R_S = \frac{k\, k_T\, P_T\, P_{H2}}{1 + K_T P_T + K_{H_2S}\, P_{H_2S}}$$

$$R_B = \frac{k'\, K_B'\, P_B\, P_{H_2S}}{(1 + K_B'\, P_B + K'_{H_2S}\, P_{H_2S})} \quad ,$$

where k, k' are the reaction rate constants; K, K' are absorption equilibrium constants; and P is partial pressure. Subscripts T and B are for thiophene and butane. R_S is the rate of thiophene disappearance, and R_B is the rate of butane formation. Thiophene adsorption on the catalyst surface occurs as a unimolecular layer with a flat orientation of the adsorbed molecule.140)

In another study with model sulfur and nitrogen compounds, it was shown that pyridine HDN is more difficult than thiophene HDS. At the conditions studied (425 C, 11.1 atm.), there is a thermodynamic limitation on the first step of the HDN reaction mechanism, in which the pyridine ring is saturated to piperidine. Sulfur compounds have a dual effect on the HDN mechanism. At low temperatures, thiophene inhibits the reaction which is postulated to occur by being in competition with pyridine for hydrogenation sites on the catalyst, retarding the hydrogenation of pyridine to piperidine and thus retarding the overall reaction rate. At high temperatures the sulfur compounds enhance HDN. It is believed that there is an interaction of hydrogen sulfide with the catalyst to improve its activity for rupture of C-N bond. This increases the rate of piperidine formation, which is rate-determining at the latter condition and thereby enhances the overall rate of HDN. The results from this study substantiate the general conclusion that the conditions for nitrogen removal are generally more vigorous than those for sulfur.(141) Detailed discussions of HDS and HDN mechanisms are given in sections that follow.

It has been shown(142) that decomposition of ethyl mercaptan in the presence of hydrogen on molybdenum and tungsten disulfide occurs by three reactions: (a) a disproportionation yielding diethyl sulfide and hydrogen sulfide, (b) a dehydrosulfurization forming ethylene and hydrogen sulfide, and (c) a hydrogenolysis giving ethane and hydrogen sulfide corresponding types of decomposition which also occurred with diethyl sulfide and hydrogen. Neither catalyst showed any activity below 300 C for reactions requiring the rupture of C-C bonds. It was proposed that for the reaction

$$C_2H_5SH \rightarrow C_2H_4 + H_2S \quad ,$$

the rate-controlling step was the one which involves breaking of the C-H bond, and for reaction

$$C_2H_5SH + H_2 \rightarrow C_2H_6 + H_2S \quad ,$$

the tungsten disulfide is more efficient as a catalyst than molybdenum disulfide.

The characterization of sulfur and nitrogen compounds in non-petroleum fuels has shown that these compounds exist predominatly as cyclic and heterocyclic hydrocarbons. Therefore the mechanisms of HDS and HDN reactions are considered individually in the following sections.

Mechanisms of HDS of Thiophene, Benzo-thiophene and Dibenzothiophene.(138,143,144) The mechanism of thiophene HDS over sulfided catalyst proposed in Reference (143) considers the reaction to be divided into three stages as shown in Figure 18. In Stage I, hydrogen-exchange reactions occur which start at 305 C when tungsten disulfide is used as a catalyst. A dissociative adsorption species, $C_4H_3S(a)$, or an associated species $C_4H_5S(a)$, is formed as an intermediate. In Stage II, the rupture of C-S bonds occurs, forming straight-chain hydrocarbons. In Stage III, a complex series of interconversions of the hydrocarbons is probable. There is evidence that the slow step in the formation of saturated hydrocarbons (butane) as pro-

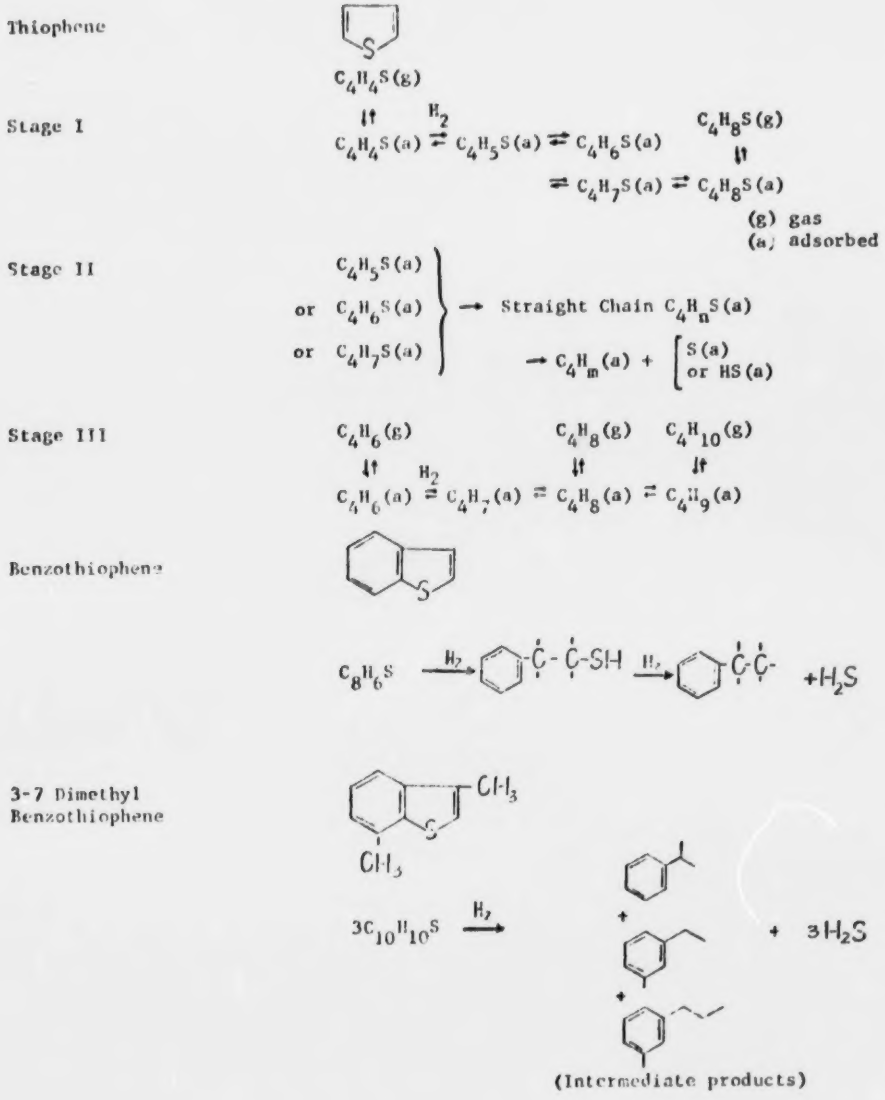

Thiophene
C4H4S(g)
Stage I
H2
C4H4S(a) ⇌ C4H5S(a) ⇌ C4H6S(a)
C4H8S(g)
⇌ C4H7S(a) ⇌ C4H8S(a)
(g) gas
(a) adsorbed
Stage II
C4H5S(a)
or C4H6S(a)
or C4H7S(a)
→ Straight Chain C4HnS(a)
→ C4Hm(a) + S(a) or HS(a)
Stage III
C4H6(g)
C4H8(g)
C4H10(g)
H2
C4H6(a) ⇌ C4H7(a) ⇌ C4H8(a) ⇌ C4H9(a)
Benzothiophene
S
C8H6S
H2
C-C-SH
H2
C-C-
+H2S
3-7 Dimethyl Benzothiophene
CH3
CH3
3C10H10S
H2
+ 3H2S
(Intermediate products)

FIGURE 18. MECHANISMS OF HYDRODESULFURIZATION (HDS) OF THIOPHENE, BENZOTHIOPHENE, DIMETHYL THIOPHENE(143,145)

ducts is the desorption of the appropriate adsorbed alkyl radical by union with a chemisorbed hydrogen atom. The molybdenum disulfide catalyst was found to have lower hydrogenation activity than tungsten disulfide. The deactivation of the molybdenum disulfide catalyst was considered to be due to the formation of strongly held and substantially dehydrogenated species, possibly polymeric in nature, on the catalyst.

In another study,(144) the mechanism of thiophene HDS is considered as "intramolecular dehydrosulfurization" analogous to alcohol dehydration to form an olefin. There are experimental data to show that by this mechanism, the hydrogen contained in the hydrogen sulfides comes from the carbon atom adjacent to the sulfur atom.

The study of the desulfurization of benzo[b]thiophene(145) over cobalt molybdate catalyst showed that desulfurization may occur by a sequence involving cleavage of one C-S bond to give a mercaptan, followed by cleavage of the second bond to give ethylbenzene as shown in Figure 18. The true catalytic nature of the reaction is based on the thermal stability of benzothiophene on nonacidic alumina at 400 C and the lack of any reaction at 400 C in the presence of nitrogen. The experimental data showed that the relative ease of hydrogenolysis of the C-S bonds of aryl mercaptans and alkyl mercaptans appeared to be about the same. In the absence of hydrogen, however, the alkyl carbon-sulfur bond would be broken preferentially since ethyl phenyl sulfide over alumina in nitrogen gave phenyl mercaptan. Further, if a stepwise process does occur, it was concluded that C-S bond cleavage would not be selective. The products of HDS of 3,7-dimethylbenzo[b]thiophene are shown in Figure 18 The following conclusions were made from the results of the study,(145) (a) the conversions, product distribution, and HDS selectivity were found to be highly dependant on the position and number of attached methyl groups, (b) the greater the number of methyl groups, the lower the conversion of dibenzo[b]thiophene to an intermediate, (c) the desulfurization step involves C-S bond breaking and no evidence was found of C-C bond breakage, (d) the aromatic ring saturation is not necessary before aryl-S bond breaking occurs.

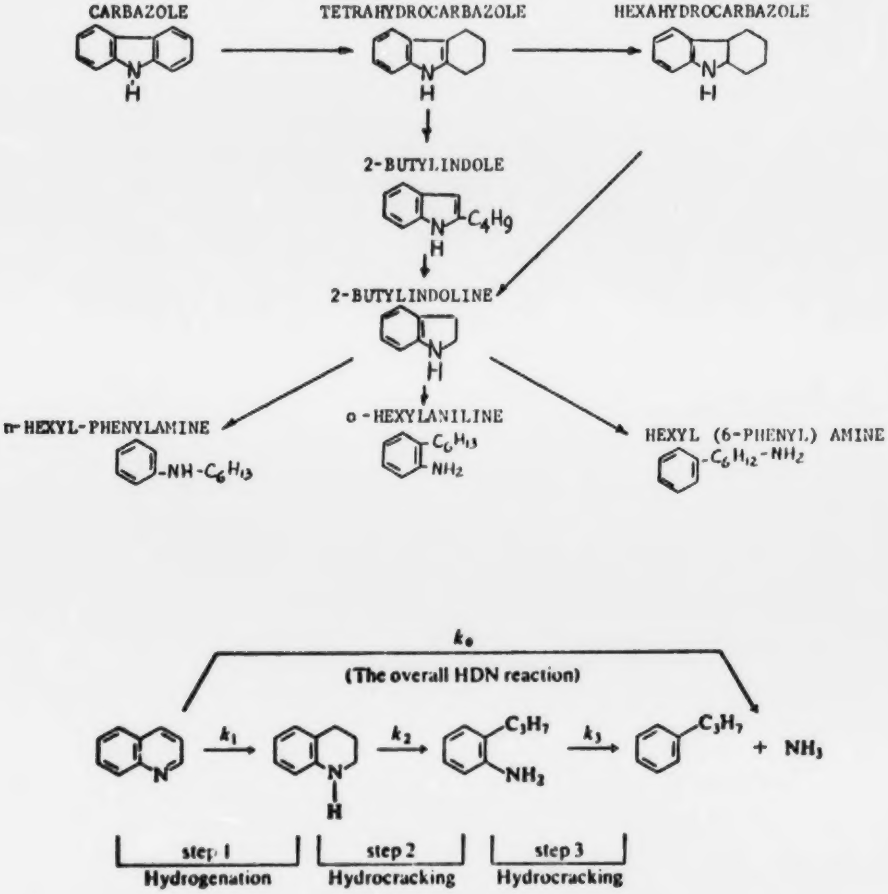
Bartsch(146) concluded that hydrogenation of an aromatic ring adjacent to the thiophenic one was not necessary in order to obtain sulfur removal. The dibenzothiophene required three times as much catalyst as benzothiophene for equivalent HDS reaction. The reaction was found to be first order with respect to the partial pressure of thiophenic compound,(146) and the rate of thiophenic disappearance is given by

$$\nu = \frac{-dp_S}{dt} = k \ p_S p_H^n$$

where P_S is partial pressure of sulfur compound; p_H is partial pressure of hydrogen; n is order with respect to hydrogen; and k is the rate constant.

Mechanism of HDN(139,141,147,148). It has been proposed that HDN of fuels occurs through a mechanism which is similar to HDS. To obtain nitrogen removal, a saturation of aromatic type, resonance-stabilized structure, is required. The hydrogenated intermediates of carbazole and quinoline and the reaction schemes are given in Figure 19. In the case of quinoline, the first hydrogenation reaction is the fastest and the first hydrocracking reaction is the slowest.(148) Flinn, et al.,(147) determined that the basic nitrogen compound, quinoline, is by far the most difficult to decompose during hydrogenation in comparison with aniline, N-butylamine, and indole. The results showed further that at high levels of HDN, the rates or removal of indole and amines fall off markedly and approach that of quinoline. This is due to the formation of quinoline from the partial HDN and hydrocracking of indole.It is proposed that alkyl groups from some minor hydrocracking reaction are present, and these alkylate an activated indole fragment to give a molecular framework containing more carbon atoms than the original indole. Such structures lead to quinolines and carbazoles in varying states of saturation.

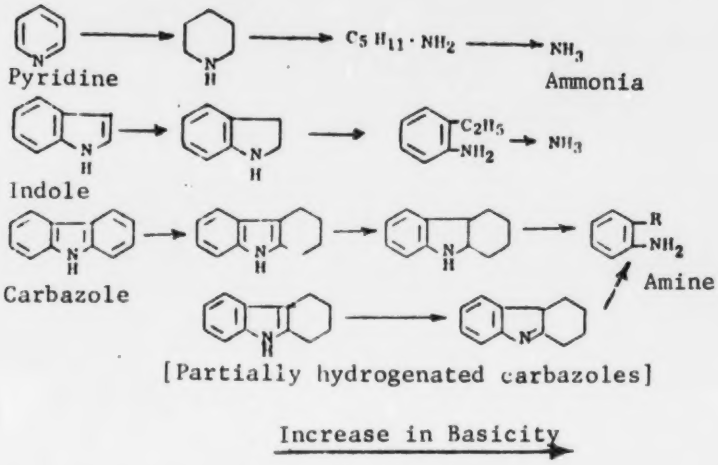
HDN reactions are more complicated than HDS reactions because with partial hydrogenation there is the change from nonbasic to basic nitrogen compounds or an increase in basicity of compounds like indoles, carbazoles, and pyridine as shown on Figure 20. The adsorptivity of nitrogen bases on metals has been related to the electron density on the ring. The lower the ionization potential of the nitrogen bases, the stronger is the coordination bond between the base and the metal surface. The basic hydrocarbons formed are strongly adsorbed (chemisorbed) on the acidic sites of the hydrocracking catalysts. This leads to catalyst deactivation. Besides the basicity of nitrogen intermediates, the size of the alkyl groups on the aromatic rings


CARBAZOLE
TETRAHYDROCARBAZOLE
HEXAHYDROCARBAZOLE
2-BUTYLINDOLE
C_4H_9
2-BUTYLINDOLINE
n-HEXYL-PHENYLAMINE
$NH-C_6H_{13}$
o-HEXYLANILINE
C_6H_{13}
NH_2
HEXYL (6-PHENYL) AMINE
$-C_6H_{12}-NH_2$
k_0
(The overall HDN reaction)
k_1
k_2
k_3
C_3H_7
NH_2
$+ NH_3$
step 1
Hydrogenation
step 2
Hydrocracking
step 3
Hydrocracking

$$k_2 = 4.416 \times 10^3 \, e^{-24700/RT} \, s^{-1}$$
$$k_3 = 5.728 \, e^{-14180/RT} \, s^{-1}$$
$$k_0 = 1.478 \times 10^5 \, e^{-28590/RT} \, s^{-1}$$

where k_2, k_3, k_0 are the rate constants

FIGURE 19. HYDROGENATED INTERMEDIATES IN CARBAZOLE AND QUINOLINE HDN(147,148)


Pyridine
$C_5H_{11} \cdot NH_2$
NH_3
Ammonia
Indole
C_2H_5
NH_2
NH_3
Carbazole
R
NH_2
Amine
[Partially hydrogenated carbazoles]
Increase in Basicity

Nitrogen Compounds Listed in Order of Basic Strength

Compound	*pKa* (H_2O)
Ammonia	9.27
Imidazole	7.03
2-Methylpyridine	6.5
Acridine	5.60
Pyridine	5.23
5,6-Benzquinoline	5.15
Isoquinoline	5.14
Dimethylaniline	5.10
6,7-Benzquinoline	5.05
Quinoline	4.94
N-Methylaniline	4.78
3,4-Benzacridine	4.70
2,3-Benzacridine	4.52
1,10-Phenanthroline	4.27
7,8-Benzquinoline	4.25
2,2′-Bipyridine	4.23
Quinazoline	3.51
Phthalazine	3.47
1,2-Benzacridine	3.45
Phenanthridine	3.30
4,7-Phenanthroline	3.12
1,7-Phenanthroline	3.11
Cinnoline	2.70
Pyrazole	2.53
Thiazole	2.53
Pyridazine	2.33
Benztriazole	1.6
Pyrimidine	1.30
Indazole	1.3
Phenazine	1.23
Diphenylamine	0.85
Quinoxaline	0.8
Pyrazine	0.6
Pyrrole	0.4
Indole	..
Propionitrile	−0.8
Carbazole	< −1

FIGURE 20. NITROGEN COMPOUNDS AND BASICITY(149)

of the nitrogen compound, e.g., carbazole, could sterically inhibit the interaction of the nitrogen-containing portion with the catalyst.

2.3.4 Mineral Matter and Trace Elements

After liquefaction of the coal, the ash minerals and any unreacted coal are separated from the liquid product by techniques discussed earlier. Sulfide minerals, that make up inorganic sulfur components of coal, inparticular pyrites, were postutated(150) to be removed during coal liquefaction by the following reactions:

$$FeS_2 + H_2 \longrightarrow FeS + H_2S \text{ (Reaction A).}$$
$$FeS + H_2 \longrightarrow Fe + H_2S \text{ (Reaction B).}$$

The equilibrium constants at coal-liquefaction temperatures for Reaction A and Reaction B are 10^2 and 10^{-3}, respectively.(150) This suggests that Reaction B may not be a significant reaction in coal-liquid desulfurization. Therefore the principal product from reaction should be FeS which is insoluble in the coal liquid would be removed with the other insoluble mineral matter.

Trace-element analysis of oils produced by both catalytic and noncatalytic liquefaction of coals by hydrogenation have been reported, as well as analyses of the feed coal and the solid residue removed by filtration.(151,152,153) Two of the coals listed in Table 35 were treated in a continuous flow reactor while the third was hydrogenated in a batch autoclave.(151) In all of the runs, coal was processed at 400 C and 3000 psi pressure of hydrogen. A proprietary catalyst was used (Gulf Research & Development Company). The vehicle in the autoclave experiment was hydrogenated phenanthrene, while in the continuous reactor, distillates from previous experiments were used. The vehicle-to-coal ratio was 2 to 1. For each coal, a major amount of the trace metal remains in the residue. High levels of titanium in the coal liquid were postulated to be due to organotitanium compounds.(151) Sodium (and calcium) levels are higher than desired for a fuel oil. The sulfur content of the oils 0.1 to 0.2 percent, is acceptable for fuels but the nitrogen content was about 0.6 percent. The elements Tl, Bi, Ge, and Ga were sought but were not detected in a low-temperature (~150 C) ash of the oil, whereas determination of Hg, Se, F, and Cd in oil had not yet been made.

TABLE 35. CONCENTRATION (PPM) OF TRACE ELEMENTS IN FEED COALS AND OILS AND RESIDUES FROM CATALYTIC LIQUEFACTION(151)

Trace Element	B Seam King Mine, Utah[a]			Lower Dekoven Seam Will Scarlett Mine, Ill.[b]			Mining City Seam Jerry Mine, Ky.[c]		
	Feed	Residue	Oil	Feed	Residue	Oil	Feed	Residue	Oil
Boron	12	25	0.15	25	150	0.12	7	40	8.03
Cobalt	25	12	0.12	12	40	0.01	4	20	0.004
Vanadium	12	25	0.06	50	150	0.25	4	40	0.004
Nickel	12	5	0.15	25	80	0.08	4	20	0.03
Titanium	75	150	5	400	1100	6	450	240	0.5
Molybdenum	Trace	25	0.08	12	40	0.01	4	20	ND
Sodium	5000	1000	5	2500	8000	2.5	150	800	0.9
Lead	ND[d]	ND	0.02	ND	ND	ND	ND	ND	ND
Zinc	25	50	0.12	125	-	0.12	ND	100	0.05
Manganese	12	25	0.05	125	300	0.12	4	80	0.05
Chromium	25	25	0.05	25	80	0.12	<1.5	20	0.05
Copper	12	25	0.02	25	90	0.03	7	40	0.01
Cadmium	0.2	0.5	-	4	4	-	1.4	2.7	-
Beryllium	0.4	0.8	0.0004	0.8	2	0.01	0.2	2	0.0009

(a) Feed:
Mineral matter
dry basis, 12.9%
Total sulfur, 0.52%
Pyritic sulfur, 0.13%
Oil: Ash, 150 ppm

(b) Feed:
Mineral matter, 25%
Total sulfur, 5.2%
Pyritic sulfur, 4.0%
Oil: Ash, 250 ppm

(c) Feed:
Mineral matter, 7.3%
Total sulfur, 3.9%
Pyritic sulfur, 0.13%
Oil: Ash, 90 ppm

(d) ND = Not detected.

Since weights of product residue were not specified, a balance could not be determined.

The distribution of trace elements in the fractions produced during noncatalytic liquefaction of coal (Solvent Refined Coal Process) are given in Table 36. The trend is for most of the trace elements to remain in the residue or solids removed from coal liquid. Elements such as Be, B, Ti, which are known to be closely associated with organic portion of coal are found in liquid fraction. The elements calcium, sodium and magnesium are present in the liquid phase at levels anticipated from its ash content.(152) On the other hand, some of the trace elements appear to be associated with the coal liquid fraction at levels that suggest concentrations exceeding those anticipated from the ash content of the liquid. These elements appear to be Co, Cr, Cu, Fe, Mn, Ni, Sn and V. Nickel and vanadium may be attributed to the porphyrin compounds while the other elements were postutaled as being part of the carbonaceous molecules of the coal.(152) As material balances for the SRC process are perfected, the fate of the trace elements should be resolved. References to approaches aimed at reducing specific trace element concentrations in SRC have not been found.

2.4 Chemical Refining Methods of Contaminant Removal

The usual concept of chemical refining of coal for the purpose of removing the contaminants involves the treatment of coal with reagents that convert the impurities into a soluble form, usually water soluble, which can be removed by leaching. In all these processes the reagents must come in contact with the contaminant. Normally the slow penetration of the reagents into large coal particles is enhanced by size reduction of the coal prior to treatment. The extent of size reduction necessary for effective treatment and the handling and economic penalties for consequences of processing very finely sized coal are important trade-offs. When aqueous leaching is employed, the problems of drying are always present, as in any process using water. Another concept of chemical refining of coal is to dissolve the coal in organic solvents so as to liberate the mineral impurities to such an extent that physical separation might be carried out. Since the solubilization of coal requires reactive solvents,

TABLE 36. CONCENTRATION OF SOME ELEMENTS IN SOLVENT REFINED COAL PROCESS FRACTIONS (in ppm)

Element	Sample No. 1[(a)]		Sample No. 2[(b)]		
	Coal Feed	SRC Product	Coal Feed	SRC Product	Filter Cake
Antimony	10.6	0.25	0.6	0.07	01.3
Arsenic	19.0	1.4	11.8	1.0	18.6
Beryllium	0.9	0.7[(c)]	-	-	-
Boron	94	100[(c)]	-	-	-
Bromine	-	-	6.9	-	8.2
Calcium	3400	180[(c)]	-	-	-
Cobalt	17	2.2[(c)]	3.7	0.31	12.8
Copper	6	3.7[(c)]	-	-	-
Chromium	38	1.3	14.0	2.68	56.4
Iron	24,000	98[(c)]	17,300	700	57,000
Lead	8	<2[(c)]	-	-	-
Nickel	29	2.5[(c)]	20	2.7	51.5
Potassium	1790	5	1,900	100	7000
Selenium	7	2	0.13	0.12	8.1
Sodium	367	30	-	-	-
Tin	104	31	-	-	-
Titanium	460	300[(c)]	-	-	-
Vanadium	175	17[(c)]	-	-	-

(a) Data from Reference 152; no data available on residue.

(b) Data from Reference 153

(c) Analysis by atomic adsorption; others by instrumental neutron activation analysis.

this approach to contaminant removal is included in this section. Size reduction and solvent recovery are important elements of processes employing this approach.

2.4.1 Dissolution and Aqueous Leaching Methods

Determination of the chemical constitution of coal by hydrolytic reactions has been reviewed extensively.(154,155) It was postulated that since the coalification process involved the elimination of water in varying degrees to form the various ranks of coal, reversal of the process (the hydrolytic reaction) would yield considerable degradation of the coal structure into simpler units. For many organic structures, hydrolysis in either acid or alkaline medium is effective. However, for coal there were no data which indicated any hydrolytic breakdown in other than alkaline medium. Dilute hydrochloric or sulfuric acid solutions appear to be ineffective, at least at temperatures which can be reached without pressure equipment. Nitric acid attack was attributed predominantly to oxidation. The reaction of alkali of concentrations from 1N to 100 percent has been studied extensively. The solubilization of oxidized coal with alkali and reprecipitation with acid was used to prepare humic acid.(156) In either case, very little was mentioned about the effectiveness of such reagents in sulfur, nitrogen, and ash mineral removal until more recently. Similarly, little if any of the technology developed in hydrometallurgy(157) has been applied to coal-contaminant removal until recently. This includes the concept of contaminant removal by bacterial action.

The dissolution of sulfur, nitrogen, and ash mineral contaminants has been accomplished using acid, alkalis, and oxidation-reduction reagents that attack and solubilize the contaminants which then can be removed by leaching either with water or other suitable solvents. These approaches and their effectiveness as contaminant-removal means are covered individually.

Alkaline Treatment Methods. Kasehagen(158) in 1937 treated bituminous coals (16 to 20 mesh) with sodium hydroxide ranging from 1N solutions to 100 percent in an autoclave at temperatures ranging from 250 to 400 C in an attempt to reduce the oxygen content of coal so as to reduce the hydrogen demand during hydrogenation. The conditions of the treatment and their effect on the sulfur and nitrogen content are given in Table 37. The analysis of the residue formed from these treatments showed that the reduction in sulfur apparently increased as the temperature increased, at least up to 375 C. It can only be assumed that this was a reduction in organic sulfur level since the original coal values were given as organic sulfur. The maximum sulfur reduction occurred at 350 C (85 percent) with a NaOH concentration of 15N. The only condition at which the nitrogen was reduced to levels substantially below that in the raw coal was at 350 C using 10N NaOH. Modest reduction in the nitrogen level occurred using 60 and 80 percent NaOH at 350 C.

A 1:1 mixture of pure NaOH and KOH was found to be very effective in removing pyritic sulfur from bituminous coals.(159) Because of the low melting characteristics of the mixture, it was considered to have greater potential for sulfur removal treatment than the use of sodium acetate, sodium hydroxide, potassium hydroxide or calcium hydroxide. As shown in Figure 21, at temperatures between 150 to 225 C only pyritic sulfur was removed from the coal, while at temperatures above 225 C, organic sulfur was also removed. The rate of removal of pyritic sulfur was very rapid at either 250 C or 400 C. As shown in Figure 22, the reaction for pyritic sulfur removal was completed in about 5 minutes. Prolonged exposure appeared to cause a back reaction at 400 C. A coal size of minus 40 mesh is necessary for rapid removal at lower temperatures. No evaluation of the coal product for retention of sodium or potassium was reported, even though the slurried coal sample was washed with hot water until the washing was neutral. Coal recovery ranged between 89 and 94 percent. Illinois and Wyoming coals gave poorer yields and smaller sulfur reductions.(159)

Ultraclean coal used for the manufacture of electrode carbon was prepared in Germany on a pilot-scale operation by I. G. Farbenindustrie.(57,160) A planned 28-ton-per-hour (input) plant was never constructed; however, equipment had been fabricated. In this process, the sodium hydroxide solution extraction method was used for the removal of minerals (and sulfur) from a froth-flotation product feed.

The caustic soda extraction plant was designed to treat 10 tons per hour of coal containing 10 percent moisture and 0.8 percent ash.(57,160)

TABLE 37. EFFECT OF TEMPERATURE AND SODIUM HYDROXIDE CONCENTRATION ON SULFUR AND NITROGEN REMOVAL DURING AUTOCLAVE TREATMENT(158)

Variable	Sulfur, percent	Nitrogen, percent
	5N NaOH Solution	
Temperature, C		
250	0.42	2.16
275	0.32	2.15
300	0.34	1.66
325	0.15	2.12
350	0.12	2.05
375	0.22	1.83
400	0.13	1.82
	At 350 C	
Concentration		
1N	0.16	2.36
5N	0.12	2.05
10N	0.21	0.98
15N	0.10	1.94
60%	0.42	1.55
80%	0.73	1.64
100%	0.78	1.72
Original Coal	0.65 (a)	1.66

(a) Organic sulfur value.

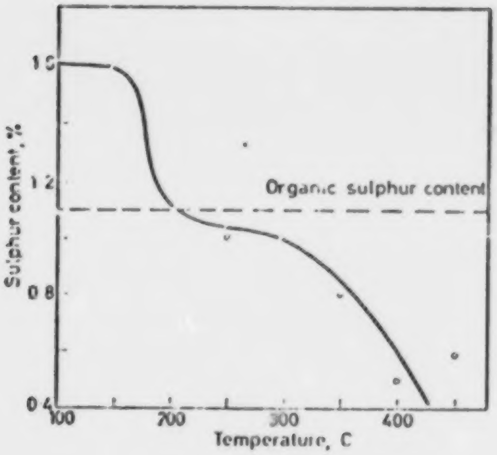


FIGURE 21. SULFUR REMOVAL WITH MOLTEN KOH-NaOH FROM MINUS 40-MESH PITTSBURGH COAL AT VARIOUS TEMPERATURES (159)

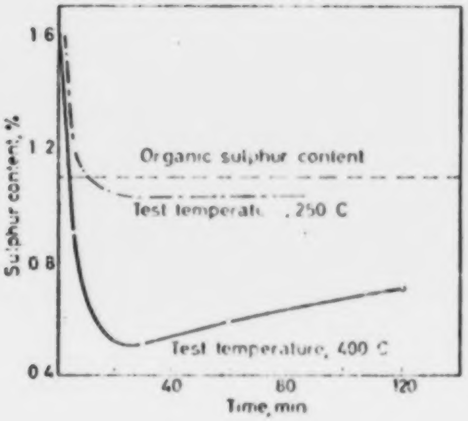


FIGURE 22. THE EFFECT OF TIME ON THE DESULFURIZATION OF MINUS 40-MESH PITTSBURGH COAL WITH MOLTEN KOH, NaOH (159)

An abridged schematic of the proposed plant is shown in Figure 23, and the flow sheet for the process is shown in Figure 24. (The numbers in Figure 24 correspond to the numbers on the equipment in Figure 23.) In the process a 3 percent solution of caustic soda was added to the extent of 40 percent of the weight of coal (40 kg solution/100 kg coal), which produced a resultant sodium hydroxide solution of 2.5 percent. The mixture was stirred at 40 to 50 C for 30 minutes and was then forced by three high-pressure paste pumps through a heat exchanger. The temperature of the paste was raised to 250 C at 100 to 200 atmospheres for a period of 20 minutes. In actual operation the paste was at an elevated temperature for 20 minutes and under pressure for 30 minutes.(57) After part of the medium's heat was removed in the heat exchanger, it was then cooled in in a water cooler and passed through pressure-reducing valves to collection pot. Softened water was added before centrifugation. The arrangement at this point allowed for recovery of the bulk of the caustic soda for reuse.

The coal at this point could not be freed of alkali even with a large number of water washings, and an acid washing stage had to be employed Without the acid treatment, the final product was an alkali-activated coke.(57) For the treatment, a 5 percent hydrochloric acid was used which was centrifuged off; the coal was then washed with water before vacuum filtration. The final product had an ash content of 0.26 to 0.28 percent. The changes in the impurity concentrations in the coal are given in Table 36.(160) The coal used in the process was chosen for its low sulfur and ash content. The chemical consumption was 21 kg of NaOH and 63.1 kg of 31 percent HCl per metric ton of extracted coal. The product was valued at 10 times the value of the raw material.(57)

The deashing of coal by the treatment of caustic followed by reprecipitation of the solubilized coal and leaching of the mineral matter with acid has been reported in Japanese and U. S. patents(161,162), and this process is similar to that developed by Germany during World War II. In the Japanese process, a coal containing 18.24 percent ash was treated mechanically to yield vitrain fraction containing <6 percent ash. The vitrain was treated with 15 percent NaOH for 2 hours at 200 C and 20 atm; it was then washed with water, followed by a 5 percent HCl washing and another water washing. The dried product (83 percent yield) contained

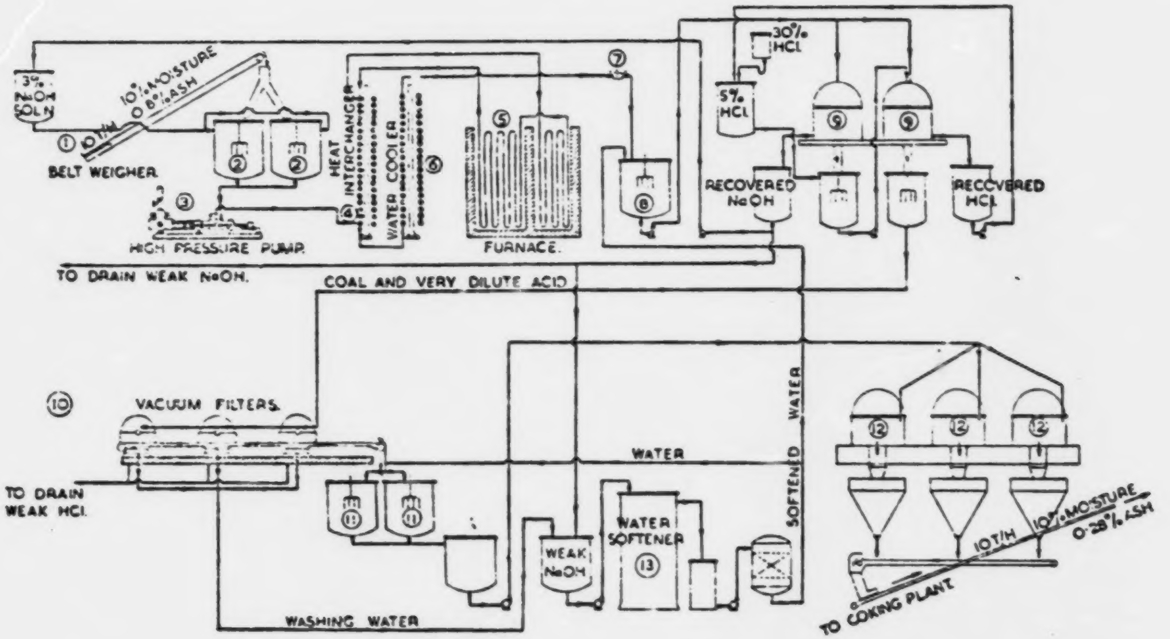

3% NaOH SOL N
10% MOISTURE
0·8% ASH
① 10 T/H
BELT WEIGHER
②
②
③
HIGH PRESSURE PUMP
④ HEAT INTERCHANGER
WATER COOLER
⑥
⑤
FURNACE.
⑦
⑧
30% HCL
5% HCL
⑨
⑨
RECOVERED NaOH
RECOVERED HCL
TO DRAIN WEAK NaOH.
COAL AND VERY DILUTE ACID
⑩
VACUUM FILTERS.
TO DRAIN WEAK HCl.
⑪
⑪
WATER
WEAK NaOH
WATER SOFTENER
⑬
SOFTENED WATER
WASHING WATER
⑫
⑫
⑫
10T/H
10% MOISTURE
0·28% ASH
TO COKING PLANT

FIGURE 23. PROJECTED PLANT TO PRODUCE ULTRACLEAN COAL BY THE USE OF CAUSTIC SODA-HYDROCHLORIC ACID EXTRACTION (57)

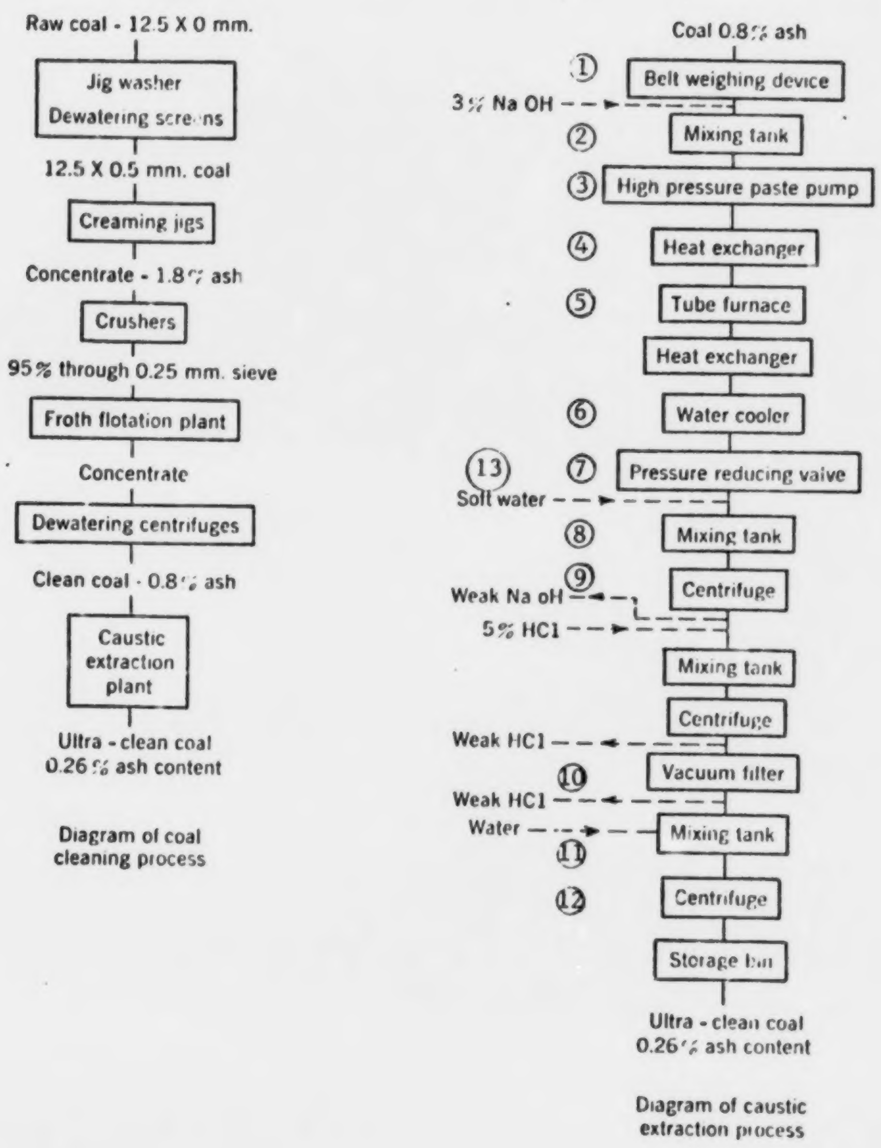

Raw coal - 12.5 X 0 mm.
Jig washer
Dewatering screens
12.5 X 0.5 mm. coal
Creaming jigs
Concentrate - 1.8% ash
Crushers
95% through 0.25 mm. sieve
Froth flotation plant
Concentrate
Dewatering centrifuges
Clean coal - 0.8% ash
Caustic extraction plant
Ultra - clean coal
0.26% ash content
Coal 0.8% ash
①
Belt weighing device
3% Na OH
②
Mixing tank
③
High pressure paste pump
④
Heat exchanger
⑤
Tube furnace
Heat exchanger
⑥
Water cooler
⑬
⑦
Pressure reducing valve
Soft water
⑧
Mixing tank
⑨
Centrifuge
Weak Na oH
5% HC1
Mixing tank
Centrifuge
Weak HC1
⑩
Vacuum filter
Weak HC1
Water
⑪
Mixing tank
⑫
Centrifuge
Storage bin
Ultra - clean coal
0.26% ash content

Diagram of coal cleaning process

Diagram of caustic extraction process

FIGURE 24. METHOD OF PRODUCING ULTRACLEAN COAL WITH CAUSTIC SODA HYDROCHLORIC ACID EXTRACTION(160)

TABLE 38. QUALITY OF GERMAN ULTRACLEAN COAL FROM CAUSTIC SODA-HYDROCHLORIC ACID EXTRACTION (PILOT-PLANT RUNS)(160)

	Percentage in		
Constituent	Raw Coal	Flotation Product	Extracted Coal
Ash	4.7	0.76	0.26
SiO_2	2.04[a]	0.22[a]	0.063[a]
Fe_2O_3	0.58	0.22	0.101
Al_2O_3	1.54	0.26	0.072
CaO	0.15	0.016	0.005
MgO	0.06	0.012	0.003
SO_3	0.12	0.008	0.0015
Alkali	0.76	0.017	0.014
TiO_2	-	0.003	0.0013

(a) Values based on ash analysis.

0.25 percent ash. In a later account of the process(163), treatment of five coals of varying rank without previous mechanical separation of the vitrain was reported. This consisted of treatment with 15 to 20 percent solutions of NaOH in an autoclave at 180 to 200 C and 18 to 20 atm for 2 to 3 hours using minus 100-mesh coal. A product with less than 1 percent ash was produced after acid treatment. The total sulfur content was reported to be unaffected. In the U. S. patented process(162), minus 200-mesh gravity-floated coal having an ash content of 0.57 percent was treated with butyl alcohol and 50 percent NaOH aqueous solution for 3 hours at 121 to 125 C. After separation and washing with 1N HCl, a product containing 0.20 percent ash was obtained.

Brooks and Sternhell reported on the effect of the use of ethanol solution of sodium hydroxide on Australian brown and subbituminous coals.(164) In two of the coals studied, total dissolution of the coal occurred without addition of new functionality to the coal. When these two coals were reprecipitated with a mineral acid, the sulfur was reduced from 1.0 to 0.7 percent and from 0.3 to 0.2 percent respectively, while the nitrogen was reduced from 0.6 to 0.5 percent in both coals. These deashed products yielded cokes even though the original coals were nonagglomerating. Solvents such as the monomethyl ether of ethyleneglycol with KOH have been used to solubilize Pittsburgh seam coal, but their effect on sulfur removal has not been reported.(165)

The use of the caustic soda solution for the removal of sulfur from high-sulfur bituminous coals has been investigated extensively by both the U. S. Bureau of Mines and Battelle Memorial Institute. In the laboratory study reported by the U. S. Bureau of Mines(166), three high-sulfur coals were investigated.

In the example given, Illinois No. 6 high-volatile bituminous coal was ground to minus 200 mesh and was treated with a solution of 24 g of NaOH in 240 ml of water for 2 hours at 225 C in a stirred autoclave, followed by acidification of the coal aqueous alkali slurry with carbon dioxide. In this treatment, pyritic sulfur was removed but the organic sulfur in the coal was apparently not attacked. The solid product recovered had an ash content higher than that of the original coal. However, if the sodium hydroxide treatment was followed by acidification with dilute hydrochloric acid or sulfuric acid (instead of CO_2), most of the mineral matter originally present was removed from the coal. Treatment with calcium hydroxide was found to be ineffective. Typical yield of treated coal was about 92 percent. Some of the results of the treatment of the Illinois No. 6 coal and two other coals are given in Table 39.

Although pyritic sulfur concentration was reduced 80 to 95 percent, there was an increase in the organic sulfur that could not be explained by the concentrating effect of ash removal. No values were given for the effect on trace elements, although with a reduction of 93 to 95 percent in the ash content of the product coal, their removal by such treatment would be expected. With treatment at 300 C rather than at 225 C, some organic sulfur is removed.(167)

Use of hydrogen and synthesis gas over pressure during treatment had no significant influence on the results, although the use of elemental sodium and hydrogen at 350 C reduced the total sulfur content of Bruceton coal from 1.25 to 0.14 percent. The use of organic peroxides and other oxidants is being investigated to improve the removal of organic sulfur from coal during the sodium hydroxide treatment.

Battelle's process which is known as the Battelle Hydrothermal Coal Process (BHCP) involves the heating of an aqueous slurry of 70 percent minus 200-mesh coal containing sodium hydroxide(168) or a mixture of sodium hydroxide and calcium hydroxide(169) at temperatures of 220 C to 340 C in an autoclave at pressures of 350 to 2500 psi. The treated coal is separated from the leachant by centrifugation, washed, and then dried to produce a solid fuel with up to 99 percent of the pyritic sulfur removed and up to 70 percent of the organic sulfur removed. The BHCP process consists of five major steps, as shown in Figures 25 and 26: (1) coal preparation, (2) the hydrothermal treatment, (3) fuel separation, (4) fuel drying, and (5) leachant regeneration. The product is now a low-ash coal as such and a portion of the sodium hydroxide used in the leaching step remains in the dried fuel. A low-sulfur, low-ash solid fuel can be produced from the alkaline-desulfurization product by treating it with dilute acid. Coal ash contents ranging from 4.6 to 13.2 percent have been reduced to 0.7 to 5.3 percent by the combined treatment. The process has been operated as a "miniplant" (a small continuous operation plant), treating 500 pounds of coal per day. The amounts of pyritic sulfur removed from five coals by alkaline desulfuriza-

TABLE 39. RESULTS OF THE TREATMENT OF COALS WITH NaOH SOLUTION AT 225 C FOR 2 HOURS FOLLOWED BY ACID POSTTREATMENT(166)

Acid Used in Posttreatment	Analysis, percent					Percent Reduction	
		Sulfur(a)					
	Ash	Total	Pyritic	Sulfate	Organic	Ash	Pyritic Sulfur
			Illinois No. 6 Coal (hvBb)				
Raw Coal	9.82	3.26	0.99	0.34	2.15(b)	-	-
CO_2	12.4	2.05	0.13	0.11	2.06	(127)(c)	87
HCl	0.67	2.54	0.11	0.01	2.44	93	89
SO_2	0.72	2.40	0.19	0.23	1.99	93	81
H_2SO_4	0.52	2.75	0.19	0.24	2.33	95	81
			Elliot Mine Coal (mvb)				
Raw Coal	18.98	4.77	3.53	0.28	1.18(b)	-	-
CO_2	22.84	2.27	0.19	0.19	2.44	(120)(c)	95
HCl	5.11	3.61	1.94	0.01	1.75	73	45
H_2SO_4	7.26	5.21	3.35	0.06	1.94	62	5
			Indiana No. 5 Coal (hvBb)				
Raw Coal	9.49	3.47	0.98	0.43	2.28(b)	-	-
CO_2	10.57	2.35	0.13	0.16	2.31	(111)(c)	87
HCl	0.48	2.63	0.06	0.02	2.56	95	94
H_2SO_4	0.72	2.56	0.15	0.20	2.23	93	85

(a) Organic sulfur values are on moisture- and ash-free basis.

(b) Raw coal values are averages of samples used.

(c) Ash value increased.

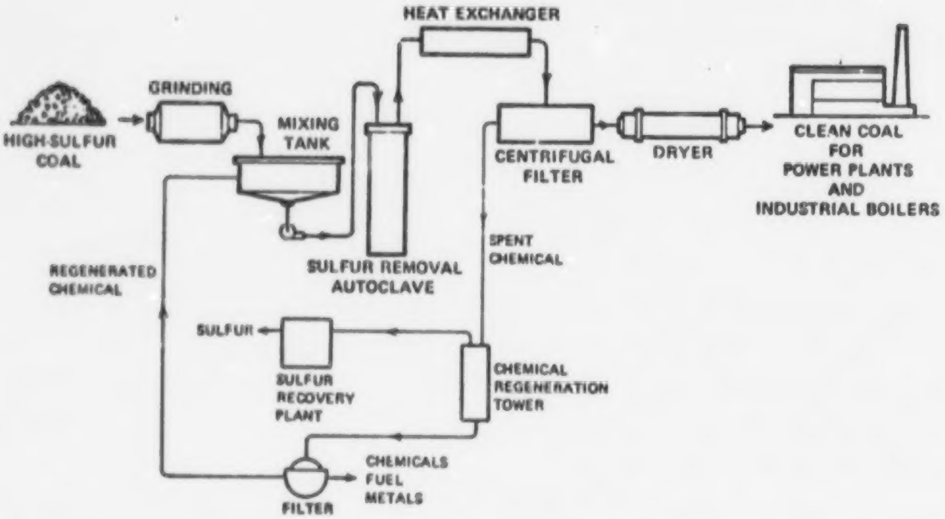

HEAT EXCHANGER
GRINDING
HIGH-SULFUR COAL
MIXING TANK
CENTRIFUGAL FILTER
DRYER
CLEAN COAL FOR POWER PLANTS AND INDUSTRIAL BOILERS
SULFUR REMOVAL AUTOCLAVE
SPENT CHEMICAL
REGENERATED CHEMICAL
SULFUR
SULFUR RECOVERY PLANT
CHEMICAL REGENERATION TOWER
CHEMICALS
FUEL
METALS
FILTER

FIGURE 25. SCHEMATIC OF THE BATTELLE HYDROTHERMAL COAL PROCESS(169)

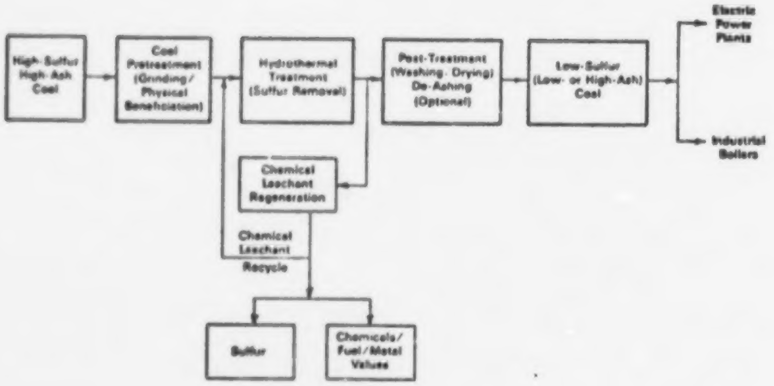

High-Sulfur High-Ash Coal
Coal Pretreatment (Grinding/ Physical Beneficiation)
Hydrothermal Treatment (Sulfur Removal)
Post-Treatment (Washing, Drying) De-Ashing (Optional)
Low-Sulfur (Low- or High-Ash) Coal
Electric Power Plants
Industrial Boilers
Chemical Leachant Regeneration
Chemical Leachant Recycle
Sulfur
Chemicals/ Fuel/Metal Values

FIGURE 26. FIVE PROCESS STEPS OF THE BATTELLE HYDROTHERMAL COAL PROCESS(169)

tion only are given in Table 40.(170) The amounts of organic sulfur removed from various coals are given in Table 41. The overall amounts of sulfur reduction for the coals studies are given in Table 42. In addition to the removal of significant amounts of aluminum and silicon, the trace elements listed in Table 43 are known to be partially removed during the alkaline desulfurization treatment.

Acid Treatment Method. Early studies on the removal of mineral constituents from brown coals with 1.5N hydrochloric and 15 percent hydrofluoric acids showed that the ash content of coal could be reduced from 5.46 percent to 0.06 percent with no retention of chloride ion.(171) The ash content of two bituminous coals was reduced from 16.2 to 2.0 percent and from 2.36 to 0.38 percent, respectively, by an identical treatment.(172)

Six thousand tons per month of ultraclean coal was produced in Germany (Baesweiler) by froth flotation followed by acid extraction of ash minerals.(57,160) The acid extraction was a batch operation in which the coal was mixed with dilute hydrochloric and hydrofluoric acids at 100 C for 1 hour. Subsequently, the coal-acid mixture was filtered and repulped twice for water washing with filtration between the washing steps. The final filtered product was dried before coking (ash, 0.65 percent). The original flotation product feed had an ash content of 0.9 percent. The overall flow sheet for the process is given in Figure 27.(160) The average analysis of ash from the high purity coke is given in Table 44.(160)

Bishop and Ward(173), during their evaluation of the determination of mineral matter in coal by the treatment with strong hydrochloric and hydrofluoric acid, found that pyrite was not affected by the treatment. The treatment with a mixture of hydrochloric acid and hydrofluoric acid followed by water washing did not increase the chloride content. The calcium content of coal was reduced to only 30 to 70 percent of that present in the original coal owing to the formation of calcium fluoride. By first treating with HCl, the amount of calcium retained was reduced to negligible amounts.

It has been reported that phosphorus as calcium phosphate in coal is solubilized in cold sulfuric acid, while the more resistant phosphorus closely associated with the coal matter can be removed only by prolonged boiling with sulfuric acid.(174)

TABLE 40. PYRITIC SULFUR EXTRACTION BY ALKALINE DESULFURIZATION (BHCP)(170)

Source of Coal			Pyritic Sulfur Analysis, % (MAF)(a)		Extraction Efficiency, %
Mine	Seam	State	Raw Coal	BHCP Coal	
CN719	6	Ohio	4.0	0.1	99
Belmont	8	Ohio	1.6	0.1	92
NE4 1	9	Ohio	4.0	0.1	99
Ken	14	Ky.	2.1	0.2	92
Beach Bottom	8	Pa.	1.7	0.1	95
Eagle 1	5	Ill.	1.5	0.2	87

(a) Moisture-ash free basis. Coal samples were supplied from the various mines.

TABLE 41. EXTRACTION OF ORGANIC SULFUR BY ALKALINE DESULFURIZATION (BHCP)(170)

Source of Coal			Organic Sulfur Analysis,[a] % (MAF)		Extraction Efficiency, %
Mine	Seam	State	Raw Coal	BHCP Coal	
Sunny Hill	6	Ohio	1.1	0.6	41
Martinka #1	Lower Kittanning	W. Va.	0.7	0.5	24
Montour #4	Pittsburgh	Pa.	1.0	0.3	70
Westland	8	Pa.	0.8	0.5	38
Beach Bottom	8	W. Va.	1.0	0.7	30
Meigs #1	4A	Ohio	2.3	1.1	52

(a) Coal samples were supplied from the various mines.

TABLE 42. COALS PRODUCED BY ALKALINE DESULFURIZATION (BHCP)(170)

Mine		Sulfur Analysis, wt %		SO_2 Equivalent lb/10^6 Btu	
		Raw Coal[a]	BHCP Coal	Raw Coal	BHCP Coal
Westland	Pitts 8 (Pa.)	1.8	0.8	2.6	1.2
Martinka #1	Lower Kittanning (W. Va.)	2.8	0.8	4.0	1.1
Renton	Upper Freeport (Pa.)	1.3	0.5	2.4	0.9
Sunny Hill	6 (Ohio)	2.3	0.8	3.9	1.2
Beach Bottom	Pitts 8 (W. Va.)	2.7	0.6	4.6	0.9
Montour #4	Pittsburgh	2.3	0.4	3.4	0.7

(a) Washed coal.

TABLE 43. EXTRACTION OF TOXIC METALS BY THE ALKALINE DESULFURIZATION PROCESS (BHCP)(170)

Metal	Concentration, ppm[(a)]	
	Raw Coal	Leached Product
Lithium	15	3
Beryllium	10	3
Boron	75	4
Phosphorus	400	80
Potassium	5000	200
Vanadium	40	2
Arsenic	25	2
Molybdenum	20	5
Barium	25	4
Lead	20	5
Thorium	3	0.5

(a) Average values for 3 Ohio coals: CN719-Seam 6, HN658-Seam 6A, and Jackson-Seam 4.

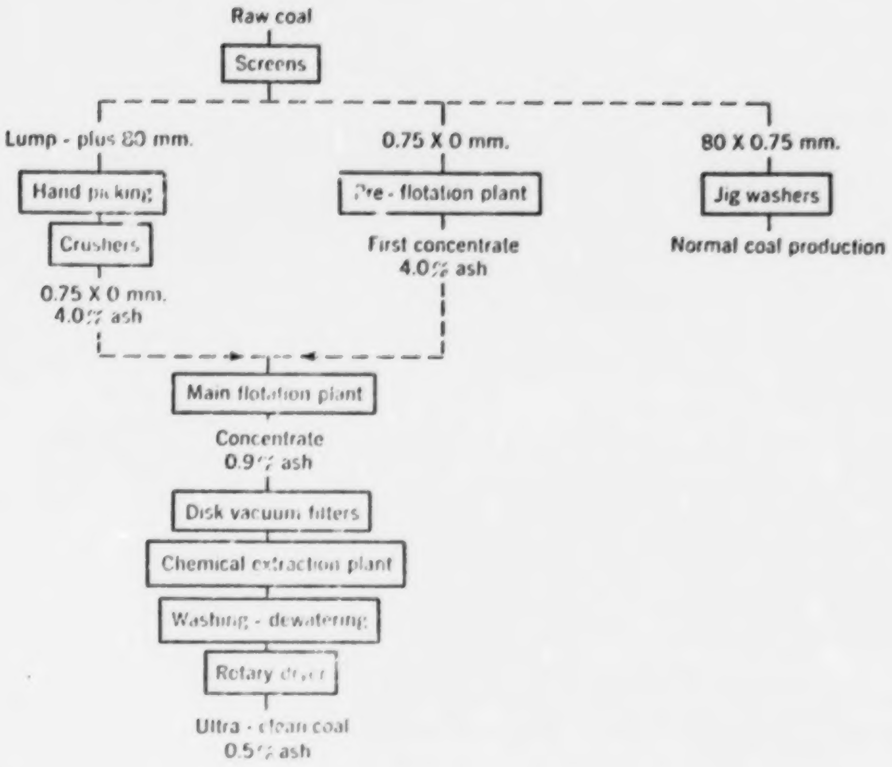

Raw coal
Screens
Lump - plus 80 mm.
0.75 X 0 mm.
80 X 0.75 mm.
Hand picking
Pre - flotation plant
Jig washers
Crushers
First concentrate
4.0% ash
Normal coal production
0.75 X 0 mm.
4.0% ash
Main flotation plant
Concentrate
0.9% ash
Disk vacuum filters
Chemical extraction plant
Washing - dewatering
Rotary dryer
Ultra - clean coal
0.5% ash

Diagram of method of producing
ultra - clean coal

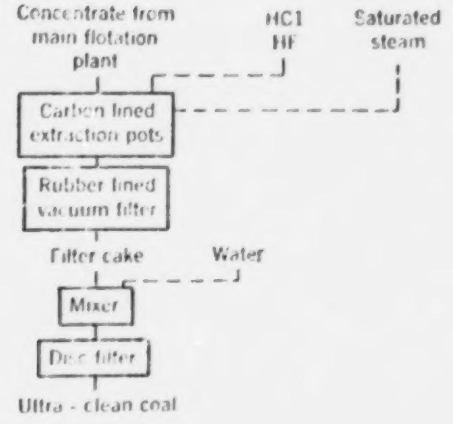

Concentrate from
main flotation
plant
HC1
HF
Saturated
steam
Carbon lined
extraction pots
Rubber lined
vacuum filter
Filter cake
Water
Mixer
Disc filter
Ultra - clean coal

Diagram of chemical
extraction plant

FIGURE 27. METHOD OF PRODUCING ULTRACLEAN COAL BY ACID EXTRACTION(160)

TABLE 44. AVERAGE ANALYSIS OF ASH FROM COKE FROM ULTRACLEAN COAL PREPARED BY TREATMENT WITH HCl-HF SOLUTION(160)

	After HCl-HF Treatment percent
Total Ash Content	0.6 to 0.7
SiO_2	46.1
Fe_2O_3	15.3
Al_2O_3	23.7
CaO	3.9
MgO	0.5
TiO_2	3.9
Sulfate (not determined)	-
Alkalies (not determined)	-

Both phosphoric acid and hydrochloric acid have been found to be effective in the removal of part of the organic nitrogen from coals.(175) With extraction times ranging from 1 to 20 hours and at temperatures from 20 to 150 C, the reductions in nitrogen content were 18 to 39 percent for Illinois No. 6 coal, 20 to 25 percent for Pittsburgh Seam coal, and 48 to 91 percent for Bervier coal. Phosphoric acid (85 percent) was considered to be slightly more effective than 20 to 30 percent hydrochloric acid.(175) Sulfonation of the coal occurred when 98 percent sulfuric acid was used. A German patent has been issued on the process.(176)

Oxidation Reaction Methods. Methods employing oxidation reactions for contaminant removal are primarily directed toward the removal of pyritic sulfur from coal. At ordinary temperatures, pyrite, i.e., ferrous disulfide (FeS_2), is an unreactive substance with very low solubility in water. However, it is rapidly attacked by oxidizing agents such as nitric acid, nitrate salts, hydrogen peroxide, hypochlorous acid or hypochlorites, and potassium chlorate. Depending on the oxidizing agent, the products are ferrous ion and either elemental sulfur or one of the sulfur oxide anions such as sulfate or thiosulfate. An important reaction used in hydrometallurgy in which ferric ions in solution are used to process sulfide ores has been used to solubilize pyrite in coal. With sulfide minerals, ferric ion (as sulfate or chloride) reacts to liberate elemental sulfur according to the reactions(157)

$$ZnS + 2Fe^{+3} \rightarrow Zn^{+2} + S$$

$$FeS + Fe_2(SO_4)_3 \rightarrow 3FeSO_4 + S.$$

With pyrite, the reaction is not quite as straightforward, but the major products are ferrous sulfate and elemental sulfur, as shown in discussions of the Meyers process of TRW below. Further oxidation of the sulfur can be brought about by reaction with oxygen but only at temperatures greater than 120 C:(157)

$$S + 1\text{-}1/2\ O_2 + H_2O \rightarrow H_2SO_4.$$

The ultimate products of the reaction are influenced by the pH of the solution. For example, in neutral or alkaline solutions, sulfides can be oxidized to thiosulfate, dithionate, or sulfoxylate ions as well as sulfate. Only at a pH of 0 to 2 is elemental sulfur one of the products.(157)

On the basis of these chemical characteristics, several approaches to the chemical alteration of pyrite in coal have been suggested(177), but only a limited number have been shown effective in a laboratory evaluation for the removal of pyrite without adversely affecting the coal matrix.

The Meyers process of TRW has been cited as such a process.(178-187) The chemistry associated with each of this process's operations has been described as follows:

Leaching: $2Fe^{+3} + (FeS_2 \cdot \text{coal}) \rightarrow 3Fe^{+2} + (2S \cdot \text{Coal})$
Sulfur Recovery: $(S \cdot \text{coal}) \rightarrow S(\text{elemental}) + \text{coal}$
Regeneration: $3Fe^{+2} + 3/4\ O_2 \rightarrow 3Fe^{+3} + 3/2\ [O^{=}]$.

The overall reaction is not this straightforward since 60 percent of the pyritic sulfur is oxidized to sulfate according to the postulated reaction(182)

$$FeS_2 + 4.6\ Fe_2(SO_4)_3 + 4.8\ H_2O \rightarrow 10.2\ FeSO_4 + 4.8\ H_2SO_4 + 0.8\ S \quad .$$

The postulated reaction for the regeneration of the ferrous sulfate solution is

$$2.4\ O_2 + 9.6\ FeSO_4 + 4.8\ H_2SO_4 \rightarrow 4.8\ Fe_2(SO_4)_3 + 4.8\ H_2O \quad .$$

The process, shown schematically in Figure 28 consists of four main sections:

- Pyrite leaching with ferric sulfate solution
- Regeneration of the leaching solution
- Coal washing with water
- Sulfur recovery by solvent extraction and coal drying.

Early laboratory and bench-scale studies were performed on four coals: Lower Kittanning, Pittsburgh Seam, Illinois No. 5, and Herrin No. 6. From these studies it was concluded that of the three crushed-coal sizes tried, minus 1/4 inch, minus 14 mesh, and minus 100 mesh, the minus 100 mesh provided the greatest amount of pyrite removal. Solutions with 3 to 10 weight percent (as ferric ion) ferric sulfate solution were capable of removing up to 90 percent of the pyritic sulfur after refluxing at 102 C for 12 hours. Continuous exchange of leach solution was required to attain such removal. Removal of up to 80 percent pyritic sulfur in 2 to 4 hours

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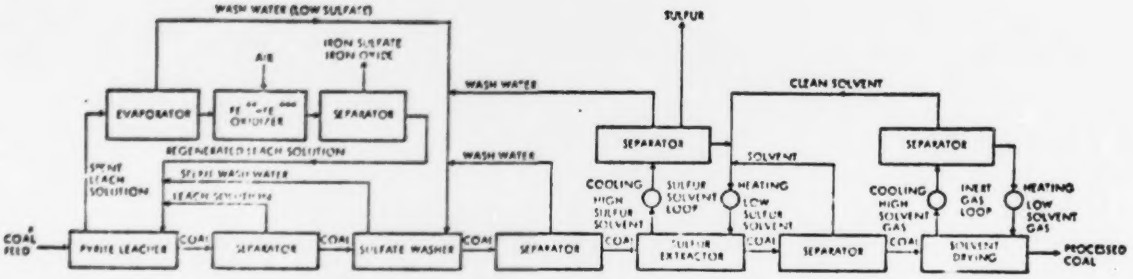

WASH WATER (LOW SULFATE)
SULFUR
IRON SULFATE
IRON OXIDE
AIR
WASH WATER
CLEAN SOLVENT
EVAPORATOR
FE^{++}→FE^{+++} OXIDIZER
SEPARATOR
SEPARATOR
SEPARATOR
REGENERATED LEACH SOLUTION
WASH WATER
SOLVENT
SPENT LEACH SOLUTION
SPENT WASH WATER
LEACH SOLUTION
COOLING
HIGH SULFUR SOLVENT
SULFUR SOLVENT LOOP
HEATING
LOW SULFUR SOLVENT
COOLING
HIGH SOLVENT GAS
INERT GAS LOOP
HEATING
LOW SOLVENT GAS
COAL FEED
PYRITE LEACHER
COAL
SEPARATOR
COAL
SULFATE WASHER
COAL
SEPARATOR
COAL
SULFUR EXTRACTOR
COAL
SEPARATOR
COAL
SOLVENT DRYING
PROCESSED COAL

FIGURE 28. MEYERS PYRITIC SULFUR REMOVAL PROCESS BLOCK DIAGRAM (180)

was indicated if the extraction was done at 120 to 130 C under pressure. The rates of removal of pyrite from minus 100-mesh Lower Kittanning coal fall off with time, indicating a dependence on the pyrite concentration.(184) In addition to the pyrite concentration, the ratio of ferric ion to iron, leaching temperature, and coal-particle top size were identified as major parameters affecting the leaching rate.

Of the options available for the removal of the sulfur from the coal that had been washed to remove sulfate, extraction with toluene or kerosene was more attractive than steam or vacuum vaporization since reaction with coal at elevated temperatures might occur to fix the sulfur in the organic matrix.(178,188)

The results from experiments at 100 C, in which the overall retention time was 8.5 hours and a complete change of the 1N $Fe_2(SO_4)_3$ leach solution occurred at 1.0 and 4.5 hours (1.2 to 1.8 liters per change) are shown in Table 45. A 1N $FeCl_2$ solution gave slightly better results but proved to be less suited to pure leachant recovery.(178,188)

In a more recent report(184), the potential of the Meyers process to desulfurize United States coal compared with physical cleaning (as evidenced by results obtained from float-sink analyses) was determined. In addition, the fate of 18 trace elements during chemical desulfurization was determined. In the laboratory study, 15 U. S. coals from mines in the Appalachian, Eastern Interior, Western Interior, and Western areas were evaluated. The conditions used in the chemical desulfurization studies were about 100 C and ambient pressure. The leach solution (1N ferric sulfate) was changed every 4 to 6 hours in order to maintain reasonable reaction rates during the extraction, which lasted 10 or more hours. All of the coals were ground to minus 100 mesh. After washing with dilute sulfuric acid and water, the wet coal was then extracted with toluene to remove the elemental sulfur. The frequency of leach-solution change depended on the coal. behavior.

The best values obtained for sulfur removal by the Meyers process are compared with values obtained for a 1.9 specific gravity float material for 11 of the coals in Table 46. The coals absent from the list were Western coals which had low initial pyritic sulfur content (i.e., analyses lacked accuracy). The calculated removals were 59 to 89 percent, even though

TABLE 45. EXTENT OF SULFUR REMOVAL BY THE MEYERS PROCESS (183)

Coal (a)	Pyritic Sulfur percent			Sulfate Sulfur percent		Total Sulfur percent		
	Initial	Final	Removal	Initial	Final	Initial	Final	Removal
Lower Kittanning	3.58	0.02	100	0.04	0.16	4.29	1.10	75
Pittsburgh	1.20	0.00	100	0.01	0.21	1.88	1.12	40

(a) Minus 100-mesh coal, 200-g samples.

TABLE 46. SUMMARY OF THE RESULTS OF PYRITE REMOVAL BY THE MEYERS PROCESS COMPARED WITH VALUES OBTAINED BY FLOAT-SINK ANALYSES(184)

	Total Sulfur in Coal[a], Percent					
Mine/Seam	Initial	Meyers Process Results	Theoretical for 95% Removal of pyrite[c]	Pyrite Conversion percent	Total Sulfur Decrease, percent	Sulfur in Coal[b] After Float-Sink, percent
Colstrip/Rosebud	1.0	0.6	0.7	83	40	--
Warwick/Sewickelgy	1.3	0.7	0.3	95	54	1.0
Jane/Lower Freeport	1.7	0.7	0.5	91	59	0.8
Orient No. 6/ Herrin No. 6	1.8	0.9	0.5	96	44	1.4
Humphrey No. 7/ Pitts. No. 8	2.5	1.4	1.1	91	44	1.9
No. 1/Mason	3.1	1.5	1.2	90	52	2.3
Fox/Lower Kittanning	3.5	1.5	0.9	89	58	2.0
Camp 1 & 2/Seam No. 9	4.2	2.1	1.8	99	50	2.9
Eagle No. 2/Ill. No. 5	4.3	2.1	1.9	93	51	2.9
Egypt Valley/Pitts No.8	6.3	2.7	1.7	93	57	4.6
Weldon/Des Moines No. 1	6.4	2.3	1.4	98	64	3.8

(a) Dry, moisture-free basis.

(b) 1.90 specific gravity float material, 14 x 0 mesh, is defined here as the limit of conventional coal cleaning.

(c) Sulfur content of coal at 95 percent pyrite removal and no increase in sulfate or measured organic sulfur content.

the pyritic sulfur values were reduced to 0.03 to 0.06 percent in the treated coals. It was concluded that near optimum conditions existed for one-half of the coals, but for the remaining coals, additional processing improvements were necessary to reach near optimum values for total pyritic sulfur removal. However, in each case the Meyers process reduced the total sulfur content to values lower than those obtainable by float-sink analysis of minus 14-mesh coals.

The nitrogen levels in the coals were found to be unaffected by the process. Of the trace elements, the process reduced the As, Be, Cr, Li, Mn, Ni, Pb, Se, and Zn contents. The reductions in trace elements for each coal are summarized in Table 47. Arsenic, manganese, and zinc are effectively removed in nearly all the coals studied. Boron, copper, and fluorine showed insignificant levels of removal.

The Ledgemont process for removing pyrite from coal employs another hydrometallurgical technique.(189) The process is designed to hasten the natural oxidation of pyrite that occurs in coal mines by increasing the rate of the reaction in water with an increase in temperature and partial pressure of oxygen. The iron sulfate and sulfuric acid values formed during the process are washed from the coal and neutralized with lime. After the solids are removed, the water is returned to the process. A block diagram of the process is shown in Figure 29. Typical conditions for the extraction and the results on Illinois No. 6 coal are given in Table 48. The advantages claimed for the oxygen process are that there is no need for elemental sulfur removal, less iron sulfate must be washed from the coal, no regeneration of leachant is required, and the reaction times are short.(189)

Removal of about 50 percent of the sulfur in bituminous coals by means of steam-air at pressures of 150 to 220 psi at temperatures up to 120 C has been reported.(190) The process involved the wet oxidation of pyrite but did not remove organic sulfur which was about 50 percent of the total sulfur in the coal

The treatment of minus 32-mesh high-sulfur coals with a solution of hydrogen peroxide and sulfuric acid was found to lower the sulfur and ash content by removing pyrite, iron, and other minerals.(191) In the study, acid concentrations ranged from 0.1N to 0.5N and the H_2O_2 concentrations

TABLE 47. TRACE ELEMENT REMOVAL DURING MEYERS PROCESS (PERCENT) (184)

	WESTERN COALS		EASTERN INTERIOR COAL BASIN			APPALACHIAN COAL BASIN				
Element	Belle Ayr	Colstrip	Eagle No. 2	Orient No. 6	Camp Nos. 1 and 2	Egypt Valley No. 21	Jane	Fox	Warwick	Humphrey No. 7
Ag	Ind[a]	Ind	Gain	Ind	50±33	50±15	N.D.	N.D.	N.D.	N.D.
As	N.D.[b]	Ind	90±17	88±3	82±9	85±6	81±7	94±5	~100	91±1
B	N.D.	86±2	N.D.	30±8	87±1	N.D.	70±2	19±9	18±25	38±9
Be	Ind	Ind	Ind	92±48	67±27	43±16	<38	70±14	N.D.	N.D.
Cd	Ind	Ind	Ind	71±45	N.D.	Ind	Ind	Ind	Ind	Ind
Cr	Gain	Gain	71±5	23±6	45±30	N.D.	60±14	58±5	41±4	N.D.
Cu	19±7	Gain	Gain	100±11	N.D.	35±9	11±4	44±6	N.D.	N.D.
F	44±9	N.D.	N.D.	14±2	N.D.	21±9	N.D.	12±2	33±6	N.D.
Hg	41±7	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	Gain	43±23	Gain
Li	Gain	Gain	Gain	78±3	90±7	N.D.	92±2	Gain	21±8	N.D.
Mn	92±25	93±3	77±7	89±10	96±3	61±2	87±7	63±6	44±4	77±5
Ni	89±6	58±5	65±10	Gain	Gain	51±5	N.D.	93±1	51±5	41±9
Pb	Gain	93±11	98±1	Gain	N.D.	67±5	99±2	Gain	38±14	N.D.
Sb	Ind	Ind	Gain	Ind	Ind	Ind	Ind	Ind	Ind	Ind
Se	N.D.	Ind	N.D.	N.D.	Ind	Ind	Ind	<85	Ind	Ind
Sn	Ind	Ind	Ind	Ind	Ind	Ind	Ind	Ind	Ind	Ind
V	Gain	93±11	N.D.	N.D.	N.D.	30±7	N.D.	Gain	N.D.	38±21
Zn	95±1	N.D.	84±1	82±4	55±18	68±4	50±21	90±1	67±2	56±14

[a] "Ind" means the element was too low to be determined in the starting coal.

[b] "N.D." means either no removal occurred or the statistical error was too large to determine the removal.

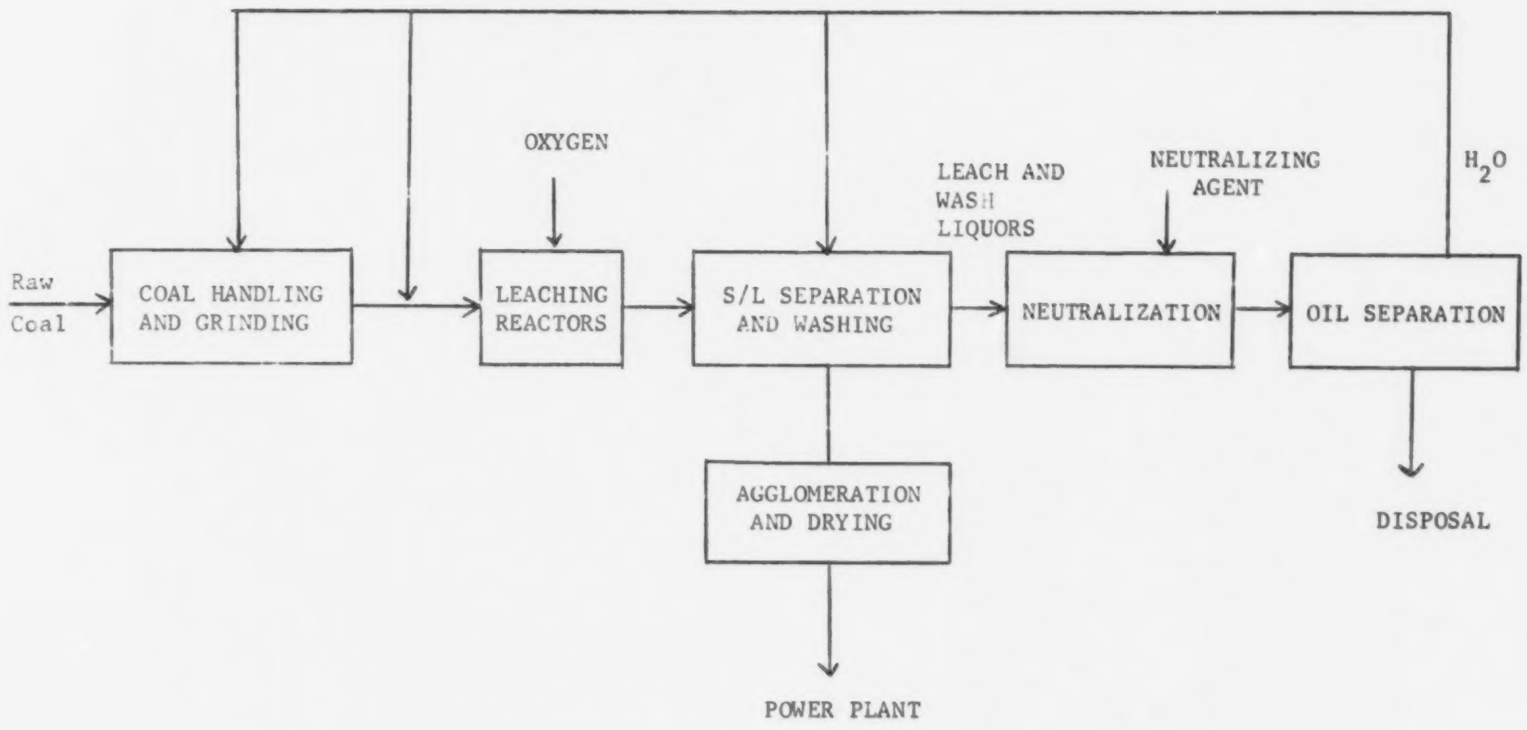

Raw
Coal
COAL HANDLING AND GRINDING
OXYGEN
LEACHING REACTORS
S/L SEPARATION AND WASHING
LEACH AND WASH LIQUORS
NEUTRALIZING AGENT
NEUTRALIZATION
H_2O
OIL SEPARATION
DISPOSAL
AGGLOMERATION AND DRYING
POWER PLANT

FIGURE 29. LEDGEMONT PROCESS FOR REMOVAL OF PYRITE SULFUR FROM COAL(189)

TABLE 48. TYPICAL RESULTS FROM LEDGEMONT OXYGEN LEACHING PROCESS (189)

Coal	Temperature, C	Oxygen Pressure, psi	Slurry Density, percent	Leaching Time, hours	Pyrite Removed, percent
Illinois No. 6	130	300	9	2	100
Illinois No. 6	130	300	19	2	99
Illinois No. 6	130	100	9	2	93

ranged from 7 to 17 percent. Treatments for 1 to 2 hours at ambient temperature had very little effect on coal composition but repeated treatments did degrade the coal slightly. Typical results of four coals, given in Table 49, indicate sulfur and ash removal only when the mixture H_2O - H_2SO_4 was used. No nitrogen was removed by the process.(191)

Microbiological Oxidation Methods. Autotrophic bacteria, which are organisms that live on inorganic matter, have been utilized to accelerate the leaching of sulfide ores.(157) In particular, Thiobacillus ferrooxidans and Ferrobacillus ferrooxidans (F. ferrooxidans) have been shown to solubilize iron from pyrite as shown in Figure 30.(157,192,193) The organisms live and grow in strongly acidic environments (pH 1.5 to 3.5) and in the presence of heavy metal ions. Maximum bacterial action occurs at 35 C. Surface-active agents in very low concentrations have been shown to increase the rate of leaching for some ores by aiding the bacteria in contacting the mineral surface. F. ferrooxidans were found to use the oxidation of ferrous to ferric ions as their energy source.(194) These organisms have been known to increase the rate of pyrite oxidation in contact with acid mine water.

Silverman, et al.,(195) reviewed the background on the use of microbial flora of acid mine waters to enhance the oxidation of pyrite of high-sulfur coal. Thiobacillus ferrooxidans have been reported to remove 23 to 27 percent of the pyrite from Donets basin (Russian) coals in 30 days. F. ferrooxidans have been found to oxidize marcasite and most pyrites, while Thiobacillus thiooxidans which normally oxidize sulfur are unable to attack pyrite but are found in acid mine waters. The study by Silverman, et al., reported on the use of F. ferrooxidans as a specific agent for the removal of pyrite from coals of different rank and the effects of acid pretreatments of coals on this process. Of the 15 coals studied, five were bituminous, four were subbituminous, and six were lignites. The results shown in Figure 31 for Kentucky No. 11 coal (12.3 percent ash and 2.1 percent pyritic sulfur) suggest that 50 percent of the pyrite was removed in 4 days, while incubation for an additional 3 days resulted in the removal of only about 10 percent more of the original pyrite. The effect on coals from other sources is shown in Table 50 under column designated as pH 3.5. The low levels of

TABLE 49. ANALYSES OF COALS BEFORE AND AFTER TREATING WITH H_2O_2-H_2SO_4 OR WITH H_2SO_4 ALONE (191)[a]

	Treating Solution[b]			Sulfur Forms, %			Heating Value, Btu/lb
Coal Seam	H_2O_2, wt %	H_2SO_4, N	Ash	SO_4	Pyr.	Org.	
Pittsburgh Seam	Untreated coal		11.7	0.06	0.74	1.00	12,990
	0	0.3	11.5	0.04	0.79	0.97	12,960
	15	0.3	10.8	0.02	0.08	1.00	13,060
Illinois No. 5	Untreated coal		9.6	0.08	1.06	2.46	12,590
	0	0.3	8.6	0.01	1.11	2.48	12,800
	15	0.3	7.5	0.06	0.09	2.55	12,860
Hastie, Iowa Bed	Untreated coal		8.6	0.48	2.05	1.57	13,300
	0	0.3	6.8	0.07	1.94	1.79	13,770
	15	0.3	5.2	0.04	0.58	1.88	14,050
Ft. Scott, Oklahoma Bed	Untreated coal		8.6	0.48	2.05	1.57	13,300
	0	0.3	6.8	0.07	1.94	1.79	13,770
	15	0.3	5.2	0.04	0.58	1.88	14,040

(a) Analyses and heating values on a dry basis.

(b) 250-ml solution per 50 grams minus 32-mesh coal; at ambient temperature for 1 hour.

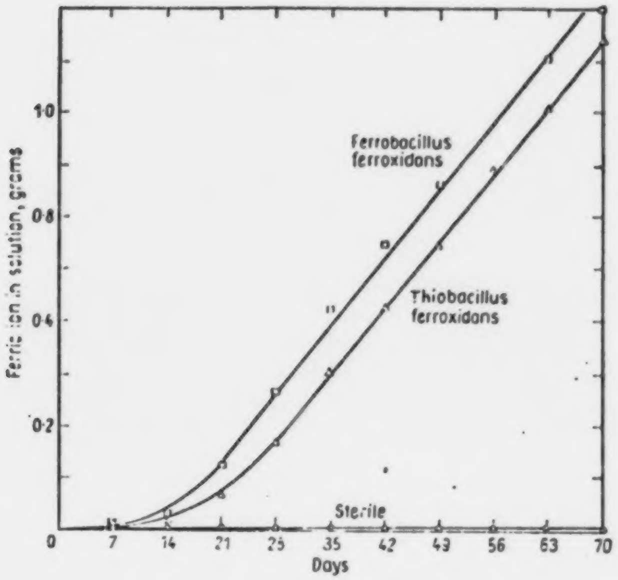


FIGURE 30. FERRIC IRON PRODUCED BY IRON-OXIDIZING BACTERIA ON PYRITE (157,192)

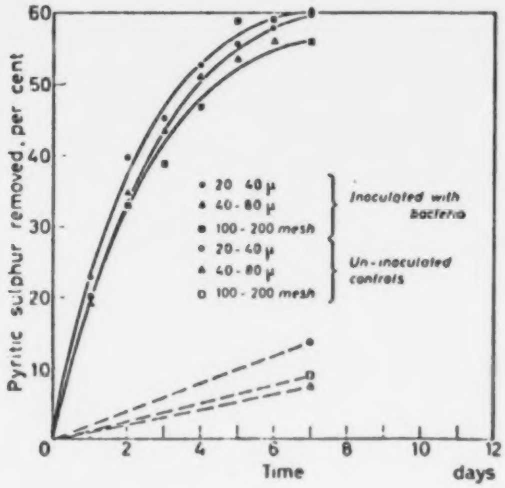


FIGURE 31. RATE OF REMOVAL OF PYRITIC SULFUR FROM DIFFERENT PARTICLE SIZE KENTUCKY NO. 11 COAL IN THE PRESENCE OF FERROBACILLUS FERROOXIDANS (195)

removal for the subbituminous and lignite were attributed to the alkaline character of the coals due to carbonate and other basic substances and their ability to keep the solutions at a pH >3.5. In order to enhance bacterial action, the use of water with a pH of 2.6, acid-treated coals, and water with a pH of 2.6 and acid treated coals plus ferric sulfate to replace that amount of iron removed during acid treatment was tried. The results obtained are also given in Table 50. Silverman, et al., concluded that when acid conditions were maintained commensurate with the physiological requirements of *F. ferrooxidans*, the pyrite in lignites, subbituminous coals and bituminous coals was susceptible to bacterial attack. The neutralizing capacity of the coals decreased with the increase in the coal rank, i.e., lignite > subbituminous > bituminous. Fine particle size was essential for high levels of removal. Since the presence of ferric sulfate was found essential for pyrite removal, the mechanism suggested for the removal by Silverman et al., was

$$\underbrace{2Fe^{+3} + FeS_2 \rightarrow 3Fe^{+2}}_{\text{F. ferrooxidans}} + 2(S) \xrightarrow[\text{F. ferrooxidans}]{O_2} 2(SO_4)^{-2} + 3Fe^{+3}$$

This suggests that the ferric ion is responsible for the solubilization of pyrite and that the sulfur thus formed is oxidized by air or the *F. ferrooxidans* to sulfate (*Thiobacillus thiooxidans* can also cause the oxidation). Therefore, it was concluded that the organism does not attack the pyrite directl but catalyzes the aerobic oxidation of ferrous ions to ferric sulfate. Mineral matter associated with the fragments of large pyrite bodies as well as trace elements associated with the fine-size pyrite and sulfide minerals would be expected to go into solution (i.e., Cr, Cu, Mn, and Ni).(196)

The action of *F. ferrooxidans* on pyrites in coal has been found useful in altering the surface properties of the mineral to facilitate its removal during immiscible fluid (spherical) agglomeration.(197) Upon grinding coal with weathered waste coal known to contain *Thiobacillus ferrooxidans* or the treatment of minus 50-micron coal with the organism for periods of 19 hours to 2 weeks, the surface of the pyrite became hydrophilic. After the pH was adjusted from about 2.5 to 5, 80 to greater than 90 percent of the pyrite was removed during oil agglomeration.(197)

TABLE 50. SUMMARY OF THE COMPARISON OF THE EFFECT OF VARIOUS CONDITIONS AND PRETREATMENTS ON THE REMOVAL OF PYRITIC SULFUR FROM BITUMINOUS, SUBBITUMINOUS AND LIGNITE COALS IN THE PRESENCE OF FERROBACILLUS FERROOXIDANS(195)

		Pyritic Sulfur Removed in 4 Days, Percent							
		Without Bacteria				With Bacteria			
Coal	Mesh Size	pH 3.5	pH 2.6	Acid Treated, pH 2.6	Acid Treated + Iron, pH 2.6	pH 3.5	pH 2.6	Acid Treated. pH 2.6	Acid Treated + Iron. pH 2.6
Bituminous									
Pittsburgh No. 8	Original Grind	--	8.6	2.7	11.0	--	57.2	43.4	60.6
Illinois No. 6	100 x 200	4.7	3.9	--	--	3.9	14.7	--	--
	200 x 325	5.5	2.3	--	--	5.4	53.6	--	--
	-325	4.8	3.5	--	--	6.2	76.3	--	--
Subbituminous									
Colorado	100 x 200	8.2	2.8	4.1	0	5.2	0	4.4	7.7
	200 x 325	7.7	2.3	0	8.2	11.7	0	6.3	23.9
	-325	6.5	3.6	14.7	1.4	3.2	0	56.0	61.4
Wyoming	100 x 200	0.2	0.7	0	0	1.2	0	0	0.5
	200 x 325	1.0	0.8	0	0	0	0.2	0	0
	-325	1.6	2.3	1.1	3.4	3.9	10.1	35.6	41.8
Lignite									
North Dakota	100 x 200	15.8	5.8	5.0	7.2	0	0	5.3	19.7
	200 x 325	0	0	5.1	6.6	0	0.8	25.2	42.1
	-325	5.6	7.5	12.1	0	1.5	3.0	37.8	58.1

2.4.2 Coal Dissolution and Organic Solvent Methods

The action of many solvents on coals has been reviewed by Dryden.(198) The extraction of coal with solvents has been used to study the constituents of coal and it was realized that yield and nature of the extract will depend on the solvent, conditions of extraction, and type of coal. Experiments that are carried out to selectively dissolve parts of coal can be successful only after a certain amount of depolymerization of the coal has occurred and, as such, some contaminants are released.

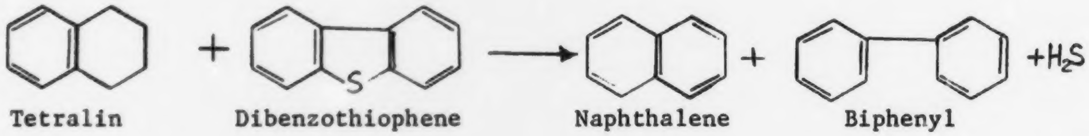
The action of solvents by dissolving coal may not result in removal of all the contaminants, but the following two significantly different products are formed upon dissolution of all or part of the coal:

Product A. The coal is converted to a liquid that can be readily processed and the ash mineral contaminants removed by filtration.

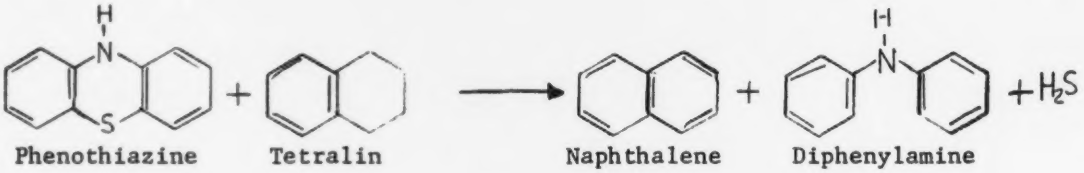
Product B. The contaminants in the coal, particularly the trace elements and some sulfur and nitrogen are concentrated in the undissolved portion of coal.

In the treatment where most of the coal is converted to a liquid, e.g., by the Pott-Broche process that was developed in Germany prior to 1944, a feedstock was obtained that easily hydrogenated to liquid fuels. The solvent and process concept used were quite similar to those being used today in the Solvent Refined Coal Processes which are discussed in the section on contaminant removal by Coal Liquefaction. The solvent is classically known as the "anthracene oil" that consists of mostly aromatic and partially hydrogenated aromatic hydrocarbons (two- and three-ring structures) and some cresols. The solubilization of the coal is attributed to the hydrogen-donation capabilities of the coal liquid. In this type of solvent extraction where a predominantly aromatic solvent is used and the major part of coal is solubilized, the trace elements which are not an integral part of coal structure are removed by filtration as the unreacted materials. It was found that during such an extraction at a Pott-Broche plant, some of the sulfur in coal was removed as H_2S and was measured at 1 to 2 g/m^3.(199) In a recent work the material balance for a proposed demonstration plant that uses a coal-derived solvent showed that the two boiler fuels produced would have sulfur contents of 0.2 percent and 0.5 percent respectively, when the feed coal has a sulfur content of 3.38 percent.(200) The organic sulfur and nitrogen contaminants dissolve in these aromatic solvents and their removal will depend upon the temperature, hydrogen pressure, and type of coal.

There has been a renewed interest in the use of hydrogen-donor reactions to desulfurize feedstocks and a process to desulfurize dibenzothiophene with tetralin would work as follows:

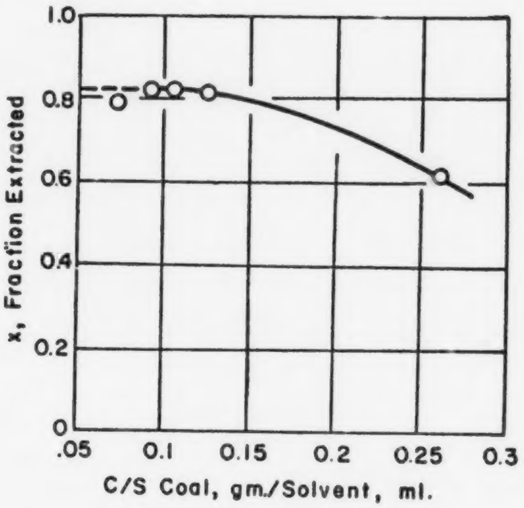


where the tetralin is dehydrogenated in the reaction. Using the same approach for phenothiazine, the reaction would be expected to produce hydrogen sulfide and ammonia. However, desulfurization was observed with tetralin but there was no nitrogen removal according to the reaction:(201)

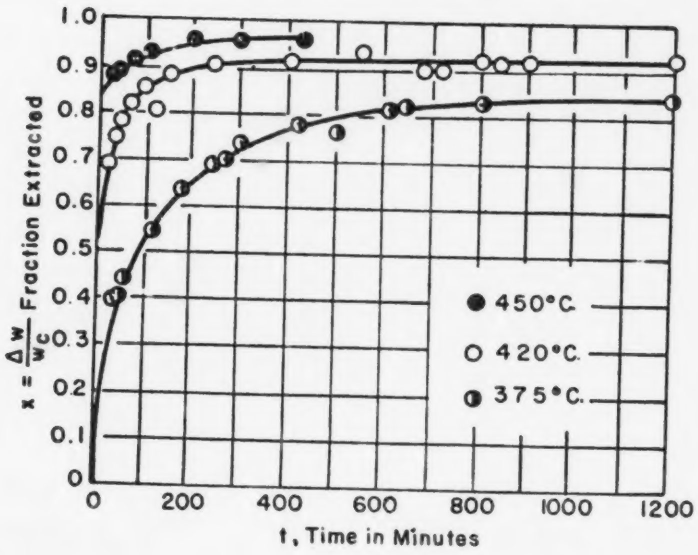


The kinetics and mechanisms of coal dissolution in a hydrogen-donor solvent, tetralin, showed that at 450 C, up to 90 percent of the coal dissolved within 50 minutes, and the ratio of the weight of coal to the volume of solvent liquid (tetralin) is shown in Figure 32. The optimum ratio of the weight of coal (grams) to the liquid volume was about 1 to 10.(202)

Solvent extraction of coal using phenanthrene-like aromatic solvents which have no hydrogen-donor capability has shown that 80 to 95 percent of the coal could be dissolved. It was found that 10 to 15 percent of the coal hydrogen exchanged with the hydrogen in the aromatic solvent and 3 to 8 percent of the aromatic solvent was chemically bound with coal.(203,204) These studies showed that coal could be solubilized in nondonor-type solvents and thus ash and trace-element contaminants could be removed by filtration.



Coal/Solvent Ratio



Thermal Dissolution of 45.71 percent
Volatile Matter Coal

FIGURE 32. DETERMINATION OF COAL TO SOLVENT RATIO AND TIME-YIELD CURVES FOR COAL DISSOLUTION IN HYDROGEN DONOR SOLVENT (202)

The selection of solvents for coal is based on many criteria, e.g., ability to swell the coal, the polar or nonpolar nature, surface tension, and internal pressure. But it has been observed that some good and bad solvents are capable of swelling the coal, and, furthermore, that the relative solvent power of two solvents may occasionally be reversed by a change in the type of coal treated.(198)

Primary aliphatic amines, pyridines, and related compounds that have an unshared pair of electrons on the nitrogen atom are effective in the extraction of coal. Other aromatic-ring compounds, naphthols, were found to be good solvents at 400 C. Between 360 and 400 C, the solvent power was found to decrease in the following order: amines, phenols, cyclic hydrocarbons, aliphatic hydrocarbons.(198)

In a study by TRW it has been reported that in two extractions of Pittsburgh coal with p-cresol, up to 80 percent of the organic sulfur was removed. As shown in Table 51, a single extraction of Beavier coal removed 29 percent of the organic sulfur, while two extractions almost doubled the removal, i.e., 54 percent.(205) The results with Pittsburgh coal were not as encouraging. Extraction of coals with less than 25 percent volatile matter with benzene-type solvents solubilized only a small amount of coal.(198) Such coals are more like an anthracite coal which is highly graphitic in nature and therefore less likely to be soluble.

Novel Approaches to Solubilize Coal. A constituent of coal, vitrain, was electrochemically reduced and the solution produced consisted of material with an average molecular weight of 800 to 900. The removal of sulfur from the vitrain took place only after the more reactive aromatic rings were reduced.(206)

A low-volatile bituminous coal, when treated with alkali metal in tetrahydrofuran in the presence of small amounts of naphthalene, was converted to a "coal anion". The coal anion was alkylated and this product was soluble in benzene-type solvents. The methylated, ethylated, and butylated derivatives were 48, 95, and 93 percent soluble in benzene, respectively. The ultimate analyses are given in Table 52. The methylated benzene-soluble fraction was ash-free and had a sulfur content of 0.06 percent compared with 0.57 and 1.9 percent of sulfur and ash respectively in the raw coal. The nitrogen content remained unchanged in these extracts.(207)

TABLE 51. SINGLE-AND DOUBLE-PASS EXTRACTION WITH P-CRESOL(a)(205)

Coal(b)	No. of Extractions	Sulfur After Extraction, percent	Organic S Removed, percent	Total S Removed, percent
Beavier(c)	1	2.69,(d) 2.71(d)	29	15
Beavier	2	2.32, 2.31	54	27
Pittsburgh(c)	1	0.82, 0.86	63	32
Pittsburgh	2	0.73, 0.74	80	40

(a) Extraction with 5 vols/wt solvent to coal for 1 hr at 200 C, filtered dried to constant wt @ 150 C/20 min.

(b) Particle size = 200 mesh.

(c) Beavier total sulfur = 3.1%, organic sulfur = 1.6%.
Pittsburgh total sulfur = 1.23%, organic sulfur = 0.61%.

(d) The two values show degree of reproducibility.

TABLE 52. ULTIMATE ANALYSIS OF ALKYLATED COAL (207)

	C	H	N	S	O	I	Ash
Original Coal	88.2	4.5	1.1	0.57	3.4	0.0	1.9
Methylated Coal	87.8	6.0	1.1	0.13	3.3	0.0	1.5
Benzene Soluble	89.4	6.3	1.1	0.06	3.0	0.0	0.0
Benzene Insoluble	85.7	5.4	1.0	0.30	4.3	0.0	3.1
Ethylated Coal	87.8	6.3	0.9	0.37	2.5	0.02	2.0
Butylated Coal	87.2	7.2	0.9	0.31	2.1	0.08	2.0

In another study, bituminous coals when acylated with aliphatic acyl chlorides using Friedel-Crafts catalysts produced materials which were up to 85 percent soluble in pyridine and other solvents. A dry steam coal and a coking coal showed particularly good reactivity.(208)

Lower rank coals in general, yield a considerable amount of extract with low-boiling solvents such as benzene, alcohol, ether, and petroleum ether. Bituminous coals with these same solvents yield much less. Exceptions to this generalization are found. (Waxes and resins are obtained from lower-rank coals.) Bituminous coals yield hydrocarbons and not acids, alcohols, ethers, carbohydrates, etc., as from peat, brown coal, and lignite. The reason for this is discussed in the volume on Coal Characterization.

The action of solvents may not selectively remove contaminants (i.e., sulfur and nitrogen organic compounds), but contaminants like the ash minerals, pyrites, and certain trace elements not associated with the coal may be removed from the solution by filtration. The solvents also help in concentrating the contaminants into fractions. Such liquid fractions may be further treated, e.g., by hydrogenation or carbonization, to remove contaminants such as organic sulfur and nitrogen. The use of certain advanced concepts, e.g., electrochemical reduction of coal or acylation, as commercial means of producing soluble contaminant-free coal will become a reality only when the many corrosive and reactive reagents used in the processes can be easily recovered and regenerated.

2.5 Contaminant Removal Via Coal Gasification

The perspective of the overall objective of this part of the study (namely the survey and evaluation of environmental control techniques for potential pollutants which have as their approach the removal of such contaminants directly from solid and liquid fuels before combustion) suggests that coal gasification is a special case of contaminant removal. It is being discussed here briefly for the sake of completeness even though the primary products are gaseous fuels of various quality. The fact that the primary products can be converted to liquid fuels (by Fischer Tropsch technology) after removal of the gaseous contaminants originating from the coal suggests that its inclusion in this survey is reasonable.

Primary gasification of coal involves the treatment of coal with air, oxygen, steam or CO_2, or a mixture of these gases to yield a combustible gaseous product. The product of the primary gasification is usually a mixture of H_2, CO, CO_2, CH_4, inerts (such as nitrogen), and minor amounts of hydrocarbons and impurities. These products are obtained from the devolatilization of coal and the reaction of the carbonaceous part of coal with the gasifying agents. The product is called a low Btu gas if an air-steam mixture is used directly to gasify the coal and it contains nitrogen as a major component. Intermediate Btu gas (or synthesis gas) is obtained when oxygen-steam mixtures are used to gasify the coal and it contains nitrogen only as a minor component. Intermediate Btu gas can be further processed to produce a methane rich gas. The required processing includes the removal of particulates, H_2S and CO_2 in downstream operations.

In the process of coal gasification, contaminants contained in the coal are released as the carbonaceous part of coal is converted to a gaseous mixture. During gasification, the sulfur and nitrogen contaminants that are part of the coal are also converted to gases, such as H_2S, CS_2, COS, SO_2, N_2, NO, HCN, and NH_3. The nature of the gases depends on the type of gasification used. These are the gaseous contaminants that must be removed from the gasifier product in downstream operations before the product gas can be utilized. The mineral matter of the coal and some of the trace elements closely associated with the minerals end up as ash, slag, or as part of the water effluents. Other trace elements and inorganic materials are volatilized or carried over during gasification. Before the gas can be utilized, these contaminants should also be removed.

The operating conditions of the gasifier determine the final form of the sulfur and nitrogen contaminants. In most cases gasification under reducing conditions favors formation of H_2S, N_2, NH_3 and HCN. Certain trace elements, such as Hg, As, Ge, Sb, and alkali metals, volatilize as metals or as various compounds depending on the reactor conditions and may be recovered with the fly ash, in water effluents, or with the by-products. Other trace metals will remain in the char residue. Some metals, e.g., Ni, Co, and Fe may be removed during gasification as carbonyls. The form of the sulfur and nitrogen contaminants in the product stream from different coal gasifiers is not expected to vary greatly because of comparable temperatures being planned or used in gasifiers.

2.5.1 Coal Gasification Processes and Contaminant Release

A material balance of a Lurgi gasifier (of the type shown in Figure 33) that used a coal with 24.03 percent ash is given in Figure 34 and shows that all the coal ash is removed as ash from the gasifier.(209)

In the case of Koppers-Totzek gasifiers, up to 50 percent of the coal ash leaves as slag at the bottom of the reactor and the rest is recovered as fly ash.(210) The Koppers-Totzek process, because of its high operating temperatures (1480 to 1930 C), has been compared to a coal combustion process with regard to certain contaminant release. Calculated molar gas composition from such a gasifier is given in Table 53. Some 80 to 90 percent of the mercury leaves with the flue gases. It has been estimated that a large portion of the cadmium and lead may also be vaporized.(211) The composition of fuel ash, slag analysis, and dust analysis for a simulated Koppers-Totzek gasifier are presented in Table 54. The distribution of the ash constituents in slag and dust is similar, and this suggests that trace elements may also be distributed similarly.

Data from batch bench-scale operations have been obtained on the decrease in trace metals in the coal as it passes through the sequence of operations in the HYGAS process. Considerable amounts of many elements, especially mercury, are lost from the coal during devolatilization and gasification (see Table 55). The loss is appreciable even during pretreating where the maximum temperature is only 430 C. Preliminary results from the HYGAS bench-scale study are summarized in Table 55 for solids leaving each processing step--the concentration being calculated on the basis of the original weight of coal.

Although elements are removed from the coal, information is needed as to where they will appear and in what form (also vapor pressure, water solubility, etc.). Such results will be needed for critical elements on all gasification processes used commercially to define what recovery or separation may be required and to allow the design of effective pollution-control and disposal facilities. It is expected that a large part of volatilized

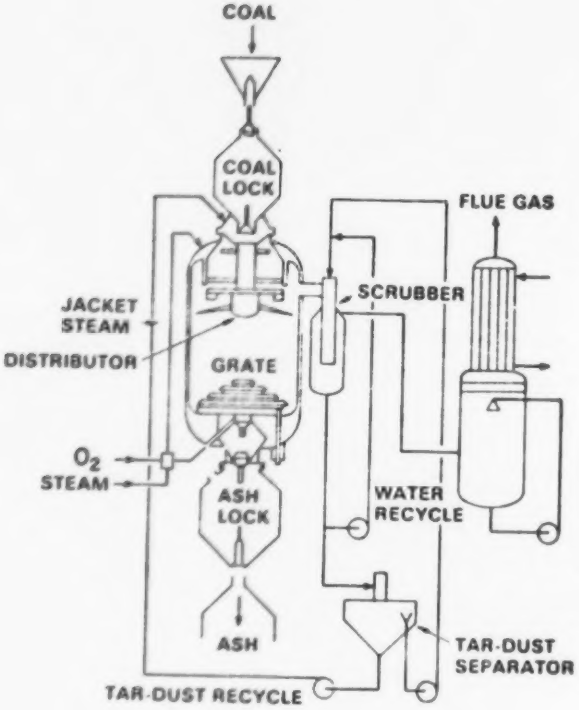

COAL
COAL LOCK
FLUE GAS
SCRUBBER
JACKET STEAM
DISTRIBUTOR
GRATE
O_2
STEAM
ASH LOCK
WATER RECYCLE
ASH
TAR-DUST SEPARATOR
TAR-DUST RECYCLE

FIGURE 33. LURGI GASIFIER

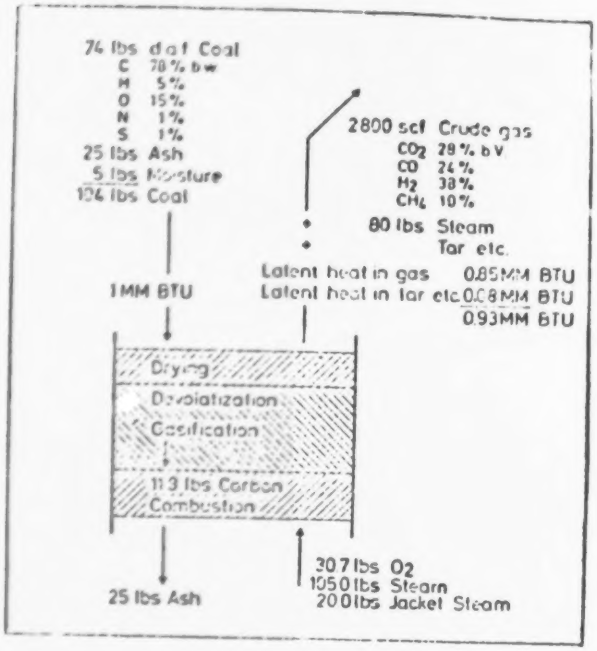

74 lbs d a f Coal
C 78 % b w
H 5 %
O 15 %
N 1 %
S 1 %
25 lbs Ash
5 lbs Moisture
104 lbs Coal
1MM BTU
2800 scf Crude gas
CO_2 28 % b V
CO 24 %
H_2 38 %
CH_4 10 %
80 lbs Steam
Tar etc.
Latent heat in gas 0.85MM BTU
Latent heat in tar etc 0.08MM BTU
0.93MM BTU
Drying
Devolatization
Gasification
11.3 lbs Carbon
Combustion
25 lbs Ash
30.7 lbs O_2
105.0 lbs Steam
20.0 lbs Jacket Steam

FIGURE 34. MATERIAL BALANCE FOR LURGI GASIFIER(209)

TABLE 53. EQUILIBRIUM MOLAR COMPOSITION OF A KOPPERS-TOTZEK GAS CALCULATED AT ENTRY TO THE WASTE HEAT BOILER(212)

Constituent	Molar Composition
	Percent
CO_2	5.49
CO	50.34
H_2	33.19
N_2	0.98
H_2S	0.32
COS	0.017
H_2O	9.64
	ppm
CH_4	1.3
SO_2	0.45
CS_2	0.12
S_2	6.00
NO	0.22
HCN	0.38
NH_3	1.38
HNCO	22.93 ppb
N_2O	Nil
NO_2	Nil
N_2O_4	Nil
HNO_3	Nil
O_2	Nil
SO_3	Nil

TABLE 54. ASH, SLAG, AND DUST ANALYSIS FOR KOPPERS-TOTZEK GASIFIER(210)

Component	Fuel Ash	Slag Analysis	Dust Analysis
Silica	41.70	46.08	30.50
Alumina	19.80	21.88	14.48
Lime	6.80	7.51	4.97
Magnesia	1.00	1.10	0.73
Iron Oxide	21.20	23.43	33.80
Carbon	--	--	--

TABLE 55. TRACE-ELEMENT CONCENTRATION OF PITTSBURGH No. 8 BITUMINOUS COAL AT VARIOUS STAGES OF GASIFICATION IN THE HYGAS PROCESS(211)(a)

	Feed Coal	After Preheat	After Hydro-Gasifier	After Electro-thermal Gasifier	Overall Loss for Element, % from Original Coal
Max Temp of Treatment C	--	430	650	1000	
Element, ppm					
Hg	0.27	0.19	0.06	0.01	96
Se	1.7	1.0	0.65	0.44	74
As	9.6	7.5	5.1	3.4	65
Te	0.11	0.07	0.05	0.04	64
Pb	5.9	4.4	3.3	2.2	63
Cd	0.78	0.59	0.41	0.30	62
Sb	0.15	0.13	0.12	0.10	33
V	33	36	30	23	30
Ni	12	11	10	9.1	24
Be	0.92	1.0	0.94	0.75	18
Cr	15	17	16	15	0

(a) Based on bench scale data.

elements will be recovered in the scrubbing operations, and whether this will result in complications or side reactions in the presence of sulfur, phenols, ammonia, ash, etc., will not be known until further information is available.(211)

The commerically proven processes or those being developed for coal gasification are partially listed on Table 56, and they are discussed in many reviews.(213) The final fate of the coal contaminants as known at this time is shown in this table. Most of the sulfur and nitrogen in coal are removed as H_2S and nitrogen gas, respectively. The trace elements show up either in the fly ash or in the slag or water. In all these gasification schemes, whether they are fixed- or fluidized-bed reactors, the final nature of the contaminants is the same. Some gasifiers operate at high temperatures and hydrogen pressures such that only reducing conditions exist, and thus H_2S and N_2 appear in the product gas.

The desulfurization of the coal during gasification by using dolomite or limestone is proving to be an effective method. The combined-cycle gasification work of Westinghouse, the CO_2 Acceptor Process (Rapid City), and gasification work by others use this concept.(213,214) It has been found that in the removal of sulfur dioxide and hydrogen sulfide, a stone (dolomite) utilization of > 77 percent was achieved within 30 minutes.(214)

$$\underset{\text{Dolomite}}{\left[\begin{matrix}\mathrm{CaO} \\ \mathrm{CaCO_3}\end{matrix} + \begin{matrix}\mathrm{MgO} \\ \mathrm{MgCO_3}\end{matrix}\right]} + H_2S \rightarrow [\mathrm{CaS} + \mathrm{MgO}] + H_2O + CO_2 \quad \left(\begin{matrix}704\ \mathrm{C} < T < 927\ \mathrm{C} \\ \text{Pressure 1 to 20 atm}\end{matrix}\right) .$$

2.6 Summary of Removal Methods

The methods of removing contaminants from coal are summarized in Table 57. When known, the general degree of contaminant removal is indicated by a + (substantial removal) or a - (negligible removal). Limitations on the types of contaminants which can be removed or the conditions under which contaminant removal occurred are specified in the footnotes. Where no data were available, blanks are left in the respective columns. Coal liquefaction by means of hydrogen and coal gasification appear to be the processes which have been proven capable of effecting substantial removal of both pyritic sulfur and organic sulfur, nitrogen and trace elements; however, the actual removal of the contaminants from the fuel components takes place in downstream operations.

TABLE 56. COAL-GASIFICATION PROCESSES AND COAL-CONTAMINANT REMOVAL[(a)]

Process, Code Name, or Acronym	Developer	Gasifier Type and Reactants	Contaminants Released/Fate
		Commercial or Advanced Processes Intermediate- or High-Btu Product	
ATGAS	Applied Technology Corporation	Molten iron; lime and coal; gasification using steam and oxygen	S: Slag as CaS N: Unknown (probably N_2, NO, HCN, NH_3) TE: Slag
BI-Gas	Bituminous Coal Research, Inc.	Fluidized: lignite and sub B coal and steam	S: H_2S N: Unknown, N_2[(c)] TE: Slag
CO_2 Acceptor	Consolidation Coal Company (CONOCO)	Fluidized: lignites, steam, and dolomite	S: H_2S (in gas; dolomite regeneration), SO_2 N: N_2 TE: Dolomite + ash
HYGAS	Institute of Gas Technology	Fluidized: hydrogasification of coal	S: H_2S N: N_2 TE: Ash/char
Molten Salt	M.W. Kellog Co.; Atomics International	Molten Na_2CO_3: coal, steam, and oxygen	S: H_2S; sulfide in salt N: N_2 TE: Molten salt, water solution
Koppers-Totzek[(b)]	Koppers Company, Inc. Pittsburgh	Entrained: coal, steam, and oxygen	S: H_2S, COS N: N_2 TE: Slag/fly ash
Lurgi[(b)]	Lurgi Mineraloltechnik GmbH Frankfurt	Fixed bed: Lignite and subbituminous noncaking	S: H_2S, COS N: N_2 TE: Ash
Hydrane	ERDA	Fluidized: hydrogasification	S: H_2S N: N_2 TE: Char/ash

TABLE 56. CONTINUED

Process, Code Name, or Acronym	Developer	Gasifier Type and Reactants	Contaminants Released/Fate
Moving Burden Ash Agglomeration	Union Carbide-Battelle (also ICI)	Fluidized: coal, ash, and steam	S: H_2S N: N_2 TE: Ash agglomerate and char
Synthane	ERDA	Fluidized: pretreated (oxidized) coal, steam, and oxygen	S: In gas H_2S; tar N: N_2 TE: Char
Winkler[(b)]	Davy Power Gas, Inc.	Fludized: coal, oxygen or enriched air and steam	S; H_2S, COS N: N_2 TE: Ash; fly ash; gas
Wellman-Galusha[(b)]	McDowell-Wellman	Fixed bed: coal, oxygen, and steam	S: H_2S N: N_2 TE: Ash/fly ash
Riley-Morgan	Riley Stoker Company	Fixed bed rotating shell: air or oxygen, coal, steam	S: H_2S N: N_2 TE: Ash
Westinghouse	Westinghouse	Fluidized bed: air steam and dolomite (combined cycle process)	S: CaS N: N_2 (probable) TE: Slag
		Mainly Low-Btu Product	
U-Gas	Institute of Gas Technology	Fluidized bed, ash agglomerating: coal, air, and steam	S: H_2S, COS N: N_2 TE: Ash
		Old and Less Known Processes	
Leuna-Wurth	Operated at Leuna (1940s)	Slagging fixed bed: low-btu gas	S: H_2S N: N_2 TE: Slag
Thyssen-Galoczy	Duisburg-Hamborn, Germany	Slagging fixed bed: low-but gas	S: H_2S N: N_2 TE: Slag

TABLE 56. CONTINUED

Process, Code, Name, or Acronym	Developer	Gasifier Type and Reactants	Contaminants Released/Fate
UGI, United Gas Improvement Company	American (1950)	Fixed bed: low-Btu gas	S: H_2S N: N_2 TE: Slag
Kerpely	British (1950)	Fixed bed: low-Btu gas	S: H_2S N: N_2 TE: Slag
Pintsch-Brassett	British (1945)	Fixed bed: low-Btu gas	S: H_2S N: N_2 TE: Slag
Caking Coal Lurgi	U.S. Bureau of Mines	Agitated fixed bed: low-Btu gas	S: H_2S N: N_2 TE: Slag
Ash Agglomerate Dilution	General Electric	Piston fed: low-Btu gas, caking coal-ash mixture	S: H_2S N: N_2 TE: Ash agglomerate
Flesch-Demag	BASF	Fluidized bed: weakly caking coal, oxygen	S: H_2S N: N_2 TE: Ash
Anthracite Gasification	Hydrocarbon Research, Inc.	Fluidized bed, low Btu gas: anthracite coal, steam-oxygen	S: H_2S N: N_2 TE: Ash
Panindco	French	Entrained: pulverized coal, preheated oxygen (or air) and steam	S: H_2S N: N_2 TE: Ash
Babcock & Wilcox Pont	Babcock & Wilcox and U.S. Bureau of Mines	Entrained: pulverized coal, steam, and oxygen	S: H_2S N: N_2 TE: Ash

TABLE 56. CONTINUED

Process, Code, Name or Acronym	Developer	Gasifier Type and Reactants	Contaminants Released/Fate
Rummel (single and double shaft)	Union Rheinische Braun-kohlen Kraftstaff	Entrained slag bath: coal, steam, and oxygen	S: H_2S N: N_2 TE: Ash
Ruhrgas Vortex	Wirbel Krammer (1940)	Coal and heated air	S: H_2S N: N_2 TE: Ash

(a) Sulfur (S), nitrogen (N), and trace elements (TE).

(b) Commercial processes.

(c) N_2 represents up to 60 percent of the nitrogen in coal; other nitrogen compounds (NH_3, HCN, NO_x) are also present.

TABLE 57. METHODS OF CONTAMINANT REMOVAL FROM COAL

	Contaminant Removal(a)			
	Sulfur			
Removal Method	Pyritic	Organic	Nitrogen	Ash Minerals and Trace Elements
I. Physical				
Gravity Differences				
Washing	+	-	-	+
Dense Media	+	-	-	+
Air Concentration	+	-	-	+
Surfacial Differences				
Froth Flotation	+	-	-	+
Immiscible Fluid	+	-	-	+
Electrophoretic	+	-	-	+
Selected Flocculation	+	-	-	+
Electrostatic	+	-	-	+
Magnetic Differences				
Thermally Treated	+	-	-	+
Unheated	+	-(b)	-	+
II. Carbonization/Pyrolysis				
Coking Processes				
Low Temperature	+	+	+	-
High Temperature	+	+	+	+(c)
With Gas Treatment				
NH_3, H_2O, CO, H_2, Air	+	+	+	
Cl_2, HCl, Br_2	+	-		+(d)
With Alkali				
NaOH, Na_2CO_3, $NaHCO_3$	-	+	+(e)	
$Ca(OH)_2$, Dolomite	+	+	+(f)	
Sodium Silicate, SiO_2	+	+	+	
Chloride Salts	+	+	+	
Al_2O_3	+	+		
With Acid				
H_2SO_4, SO_2	-(g)	-		
III. Coal Liquefaction (Hydrogenation)				
Catalytic	+	+	+	+(h)
Noncatalytic	+	+	+	+(i)
IV. Chemical Refining				
Alkali	+	+(j)	-	+
Acid	-	-	+	+
Oxidant	+	-	-	+(k)
Organic Solvent				
Reactive	+(m)	+	+(l)	+(m)
Nonreactive	+(m)	-	-	+(m)
V. Gasification				
Raw Coal	+	+	+	+(n)
With Additive, e.g., Dolomite	+(n)	+	+	+(n)

(a) Plus (+) = all or part normally > 50 percent; negative (-) = negligible removal.
(b) Slight reduction in organic sulfur observed.
(c) Over and above values observed in coal ash.
(d) After washing with water.
(e) Only for noncoking coals.
(f) Part as cyanogen, C_2N_2.
(g) Increase in sulfur retained by coke observed.
(h) Removed by filtration from liquid; trace elements deposit on catalyst; present in residue used for H_2 formation.
(i) Removed by filtration of hot liquid; present in residue used for H_2 formation.
(j) With molten alkali and long residence time; some removal noted when NaOH solution used at elevated temperature.
(k) Trace elements present as sulfides or as part of pyrite/ash mineral structure.
(l) Only with hydrogenation.
(m) Removed with insoluble portion of treated coal.
(n) Removed with ash from process except for volatile trace elements which are removed from gas stream.

3.0 METHODS OF REMOVING CONTAMINANTS FROM PETROLEUM

3.1 Physical Methods

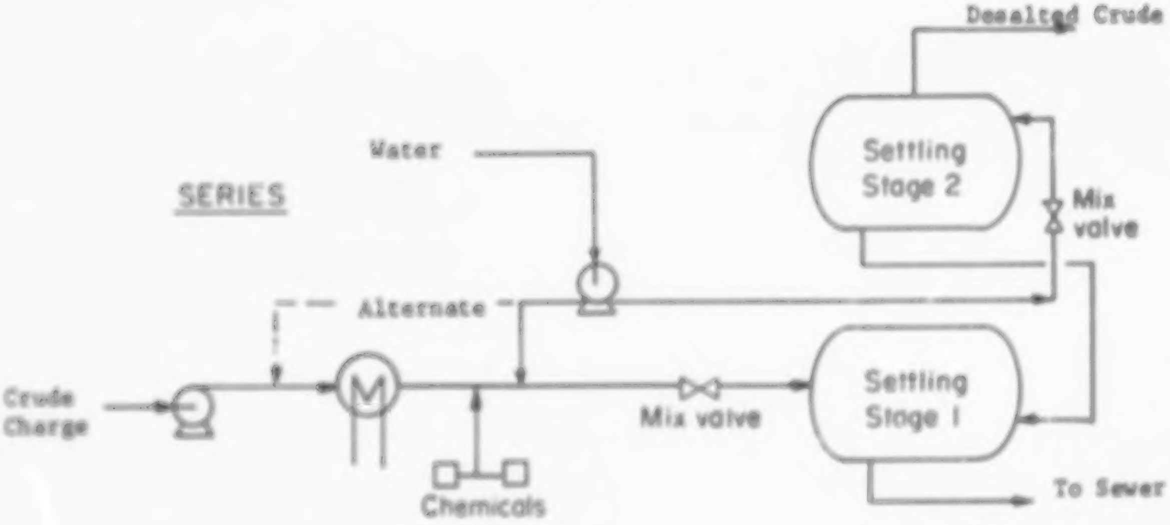
3.1.1 Water Washing

Washing of crude oil with water is a widely practiced method of desalting, i.e., removing water soluble salts, primarily NaCl. Typical flow sheets for this operation are shown in Figure 35.(215) Both flow sheets show two stages of desalting, but in the top one the stages are in series with respect to the oil whereas the bottom one they are in parallel.

The oil is heated to 90-150 C (200-300 F) at a pressure sufficiently above the mixture bubble point.(216) Higher density crudes are normally desalted at higher temperatures than are lower density crudes. The water can be added either before or after the crude-oil heat exchangers. The quantity of water required is usually 4 to 8 volume percent of the oil, although this depends on the salt content of the oil,as shown in Table 58.(217) Some chemicals are normally added to help break the oil-water emulsions which form in this process. Two stages of mixing and settling are used, with the mixing being done by mix valves and the settling in suitable vessels. The water from the second settler goes to the first settler. The oil flows through the two stages either in series or in parallel fashion. Clearly, series operation will achieve a greater degree of salt removal than parallel operation, but parallel operation permits a higher oil throughput for a given system.

In addition to adding chemicals to help break the oil-water emulsions in the settlers, it is common practice to apply an electrical field across the settlers to further aid the phase separation. This is called electrodewatering. Units which employ this technique are called electric desalters or electrostatic desalters. It should be noted that in such units the electrical force is used primarily to separate the oil and water, although it is conceivable that this force could enhance the migration of contaminants in the oil and thus affect the contaminant removal itself. In desalters that are not electric, it is common practice

SERIES


Desalted Crude
Water
Settling Stage 2
Mix valve
Alternate
Crude Charge
M
Mix valve
Settling Stage 1
Chemicals
To Sewer

PARALLEL

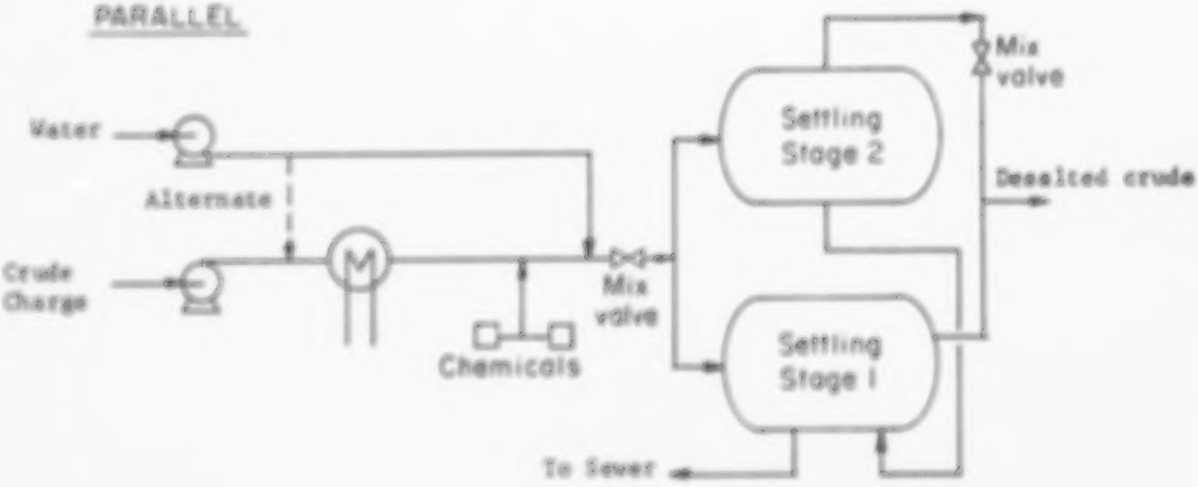

Mix valve
Water
Settling Stage 2
Desalted crude
Alternate
Crude Charge
M
Mix valve
Chemicals
Settling Stage 1
To Sewer

FIGURE 35. TYPICAL FLOW SHEETS FOR CRUDE OIL DESALTING BY WATER WASHING(215)

TABLE 58. EFFECT OF SALT CONTENT ON UTILITY REQUIREMENTS FOR DESALTING[(217)]

Inlet Salt Concentration		Water Required, vol percent of crude	Steam Required, lb/bbl of crude
g/1000 liters	lb/1000 bbl		
57	20	1	0.5
285	100	2-5	1-3
570	200	4-10	2-5
1,425	500	10-25	5-13
2,850	1,000	20-50	10-25

to pack the settling vessels with Fiberglas, excelsior, or a similar material to hasten the coalescence of droplets.(218)

The specific chemicals used and their quantities are proprietary to individual companies. The chemicals usually include some surfactants and wetting agents. The quantities added are often in the range of 3 to 12 ppm by volume on crude (1 pt-2 qt per 1000 bbl crude). The benefits obtained from the chemicals include:

- Higher degree of salt removal
- Lower total solids concentrations in product
- Reduction of trace metals such as vanadium and copper in product
- Very low or no water carryover with product.(215)

With the increasing use of water recycling in refineries, more internal water sources are being used to provide the water for desalting. Many of the possible internal water streams contain some ammonia and, fortunately, at least small amounts of ammonia have no adverse effects on the desalting operation. Water containing up to 1000 ppm of NH_3 has been used for desalting. Actually there is a benefit in that refiners often inject some caustic into the oil after the desalting to reduce corrosion rates, and the presence of NH_3 in the desalting water decreases the quantity of caustic which must be added. On the other hand, certain other impurities must be carefully stripped from the water used for desalting. An example is phenolic compounds, which will go into the oil and can poison the catalysts used in some of the downstream processing units.(215)

3.1.2 Filtration

Filtration has been used successfully to remove salts from petroleum fractions. Hemminger(219) mentions filtering crude oil at 90 to 200 C (200 to 400 F) prior to cracking operations but does not give details. Porter and Northcott(220) filtered crude oil in a bed of bauxite at 415 C (780 F) and 1000 psi pressure to remove sodium, and then added hydrogen and removed vanadium in another bed of bauxite. Their claim is only qualitative. Wiles(221) achieved a 43 percent reduction in the salt content of a Panhandle crude oil by percolating it through a 2-inch layer of anhydrous $CaCl_2$ at 65 C (150 F) and atmospheric pressure. Cerf$^{(222)}$ desalted a substantially dry, emulsion-free mineral oil by passing it through a stationary bed of rock salt. Kirk$^{(223)}$ filtered residual oil as a slurry containing 0.1 to 1.0 percent filter aid through a 40-micron porous medium. Shields,$^{(224)}$ of General Electric Company, studied the filtration of residual fuel oil, but the results of this work have not been published. However, Silverberg,$^{(225)}$ of General Electric, has published some data on this subject which is discussed here.

Silverberg repeated some of the previous experiments (listed above) without success, using a 1- by 12-inch percolating column. Tests with bauxite, $CaCl_2$, rock salt, and silica gel all failed to reduce the sodium content of residual fuel oil. Silverberg then studied the filtration of residual oil with a rotary vacuum filter and a variety of filter precoat materials, primarily forms of diatomaceous earth or perlite. Of the materials tested, the best results were obtained with a diatomaceous earth, Dicalite 4200. In this case, the sodium content of the oil was reduced from 41 to 4 ppm at an oil throughput of 144 ℓ/sq m/hr (3.53 gal/sq ft/h The calcium content was reduced from 14 to 5 ppm, and no reduction in vanadium content was observed.

Silverberg suggests the following four possible mechanisms for the removal of sodium from oil by vacuum filtration:

- Mechanical filtration of suspended sodium-containing solids by the capillary passages
- Evaporation of water by the high temperature and vacuum, accompanied by formation of salt crystals and filtering out of these crystals
- Adsorption of sodium complexes on the precoat material
- Deemulsification of salty water in the small pore passages on the outer rim of the precoat, where these droplets are the first to be scraped off.

Silverberg estimated the cost of the filtration operation to be about 20 cents per barrel of oil and thus concluded that this operation would not be economically competitive with conventional desalting by water washing.

Filtration of chilled oil has been used commercially for dewaxing of oil, but this is not considered here because the wax removed is not a contaminant in the scope of this study.

3.1.3 Centrifugation

The primary use of conventional centrifugation technology for petroleum fractions is for oil-water separations, either after water washing or to remove water which accidentally gets into the oil.(226-228) Centrifuges have even been installed on ships to purify their fuel in this regard. This is not, of course, contaminant removal in the sense of this study. However, there are cases in which conventional centrifugation is reported to remove metals other than those expected to be associated with the water which is removed (e.g., sodium). The results on this are mixed. Reference 228 reports that a solids-ejecting centrifuge removed 70 percent of the vanadium from a ship's fuel oil, reducing it from 0.2 to 0.07 ppm. This result is termed "surprising" and "yet to be explained". On the other hand, Reference 226 states that vanadium is not removed by water washing plus centrifugation. Conventional centrifugation is also used in dewaxing operations, although this is not within the scope of this study.

Other the other hand, ultracentrifugation by itself can be used to separate some contaminants from petroleum. Ultracentrifugation is a technique commonly used in separating colloidal solutions, and many of the contaminants in petroleum, particularly metals, are contained in colloidal structures.(229,230) Orlov(231) presents data on the ultracentrifugation of petroleum fractions. Most of the data were obtained at a centrifugal force of 80,000 g (g = multiples of gravitational force at earth's surface), although some data were also obtained at 250,000 g. The times of centrifugation varied from 3 to 125 hours, but most of the separation was found to occur during the first few hours. A qualitative analysis of the colloidal material separated from the oil indicated the presence of metal prophyrin compounds in this material.

3.1.4 Adsorption

Adsorption is used commercially for improving the color of petroleum products, which involves removing some trace constituents from the oil. The species removed are high-molecular-weight hydrocarbons, i.e., resinous and asphaltic substances, and hence are not contaminants in the scope of this study except to whatever extent they may contain atoms other than carbon and hydrogen. The more important groups of adsorbents used for color improvement are: (1) fuller's earth, (2) bentonite, (3) various natural and treated clays, (4) bog iron ore, (5) bauxite and alumina, and (6) activated carbon. In general, hydrocarbons are adsorbed on these materials in the order

unsaturates > aromatics > naphthenes > paraffins.

In each series, the higher-molecular-weight hydrocarbons are adsorbed more readily, which accounts for most of the decolorizing action.(231)

A study of the effectiveness of silica gel, fuller's earth, and alumina in removing sulfur species from oil was conducted by Wood.(233) In this study, solutions of various single, pure sulfur compounds in naphtha were shaken with the adsorbent and then analyzed to determine the degree of removal obtained. The descriptions of the removal efficiencies given by Wood are presented in Table 59. The results indicate that silica gel is, in general, a more effective desulfurizing agent than fuller's earth or alumina. The action of silica gel is probably due to the ease with which it adsorbs mercaptans.

Makhlitt(234,235) has studied the use of adsorption to remove sulfur, as well as aromatic hydrocarbons, from jet fuel. The sulfur-compound-group composition of a 140 to 280 C (280 to 540 F) cut (distillation) of Romashkina crude oil was determined by a silica-gel separation plus an analysis technique. Most of the sulfur compounds were found to be concentrated in a fraction containing aromatic hydrocarbons and comprising only 3.5 weight percent of the original 140 to 280 C cut. The chromatogram for separation of the 140 to 280 C cut showed that the first 90 percent of the desorbate represents a hydrocarbon mixture with low contents of sulfur and aromatic hydrocarbons. These facts indicate that adsorption should be an effective method of removing the sulfur and aromatic hydrocarbons from this cut. Adsorption tests were conducted using silica gel, NaX zeolite, and an aluminosilicate catalyst. The order of adsorptivity for the sulfur compounds in this cut

TABLE 59. DECREE OF REMOVAL OF SULFUR SPECIES FROM OIL BY ADSORBENTS(233)

Species Contained in Naphtha Solution	Adsorbent Used		
	Silica Gel	Fuller's Earth	Al_2O_3
Free sulfur	None	None	None
Isoamyl mercaptan	Removes fairly well	None	Removes sparingly
Hydrogen sulfide	None	None	Removes sparingly
Dimethyl sulfate	Removes	Removes	Removes sparingly
Methyl p-toluene sulfonate	Removes fairly well	Removes	Removes sparingly
Carbon disulfide	None	None	None
n-butyl sulfide	Removes partially	None	None
n-propyl disulfide	Removes partially	Removes sparingly	None
Thiophene	None	None	None
Diphenyl sulfoxide	Removes	Removes	Removes sparingly
n-butyl sulfone	Removes	Removes	Removes sparingly
Representative percent removal of total sulfur	48	21	6

was

silica gel > aluminosilicate > NaX zeolite.

For pure n-dihexyl sulfide, the adsorptivity of NaX zeolite was greater than that of aluminosilicate. The difference in ordering is evidently related to the fact that the sulfur compounds in the cut studied were aromatic in nature, whereas n-dihexyl sulfide is paraffinic. The time required to reach adsorption equilibrium was in the order

aluminosilicate (4 mm grain size) > silica gel (0.5-1 mm)
> aluminosilicate (0.5-1 mm).

3.1.5 Solvent Deasphalting

Solvent deasphalting of petroleum fractions was developed in the 1940's and is used rather extensively in refining, although less than in the past. In this process, a residuum is contacted with a light hydrocarbon (the solvent), such as propane, normally at a temperature and pressure near the critical temperature and pressure of the solvent. The extraction temperature is generally 65 to 120 C (150 to 250 F) and the pressure 400 to 600 psi.(236) The solvent preferentially rejects the asphaltenes, which contain most of the metals, from the residuum. The phases are then separated and the extract is flashed to recover the solvent, which is then recompressed and recycled. A typical flow sheet for this process is shown in Figure 36.(236)

Some typical data on solvent deasphalting of residua are shown in Table 60.(236-238) Although the primary objective of the process is to remove metals, it also removes some sulfur and nitrogen. The primary drawback of the process is that it removes metals by removing the entire asphaltene molecule in which most of these metals are contained. This means that some of the heavy hydrocarbon compounds which the refiner would like to sell as part of the fuel oil are recovered as an asphaltene fraction which must be disposed of in some other way. In other words, the fuel oil yield loss is considerable. As the data in Table 60 show (left and right hand pairs of columns), the degree of removal can be increased at the expense

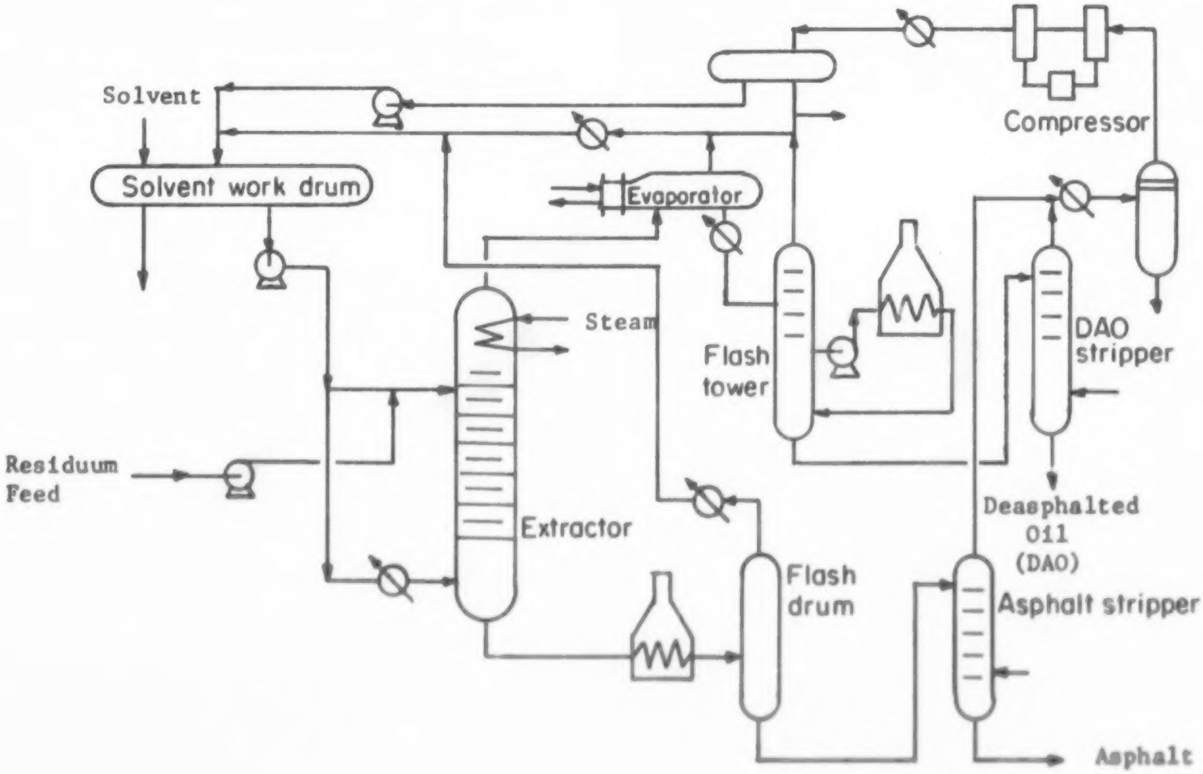

Solvent
Solvent work drum
Compressor
Evaporator
Steam
Flash tower
DAO stripper
Residuum Feed
Extractor
Deasphalted Oil (DAO)
Flash drum
Asphalt stripper
Asphalt

FIGURE 36. TYPICAL FLOW SHEET FOR SOLVENT DEASPHALTING OF OIL(236)

TABLE 60. TYPICAL DATA ON SOLVENT DEASPHALTING OF RESIDUA

Crude Oil Type	Gach Saran	Gach Saran	West Texas	California	Canadian	South American
Residuum feedstock						
Specific gravity at 16 C (60 F)	1.030	1.030	0.986	1.027	1.003	1.023
Viscosity at 99 C (210 F), SUS(a)	31,750	31,750	526	9,600	1,740	75,000
Conradson carbon residue (weight percent)	22.2	22.2	12.1	22.2	18.9	15.0
Sulfur (weight percent)	2.66	2.66				
V (ppm)	372	372	27.6	136	30.9	365.0
Ni (ppm)	120	120	16.0	139	46.6	73.6
Cu + Fe (ppm)			14.8	94	40.7	15.5
Heptane insolubles (weight percent)	10	10				
Deasphalted oil product						
Yield (volume percent of feed)	51.5	75	66.0	52.8	67.8	49.8
Specific gravity at 16 C (60 F)	0.960	0.993	0.936	0.944	0.948	0.946
Viscosity at 99 C (210 F), SUS(a)	527	2,309	113	251	250	615
Conradson carbon residue (weight percent)	6.3	14.3	2.2	5.3	5.4	5.9
Sulfur (weight percent)	1.89	2.25				
V (ppm)	8.0	89	1.3	2.3	1.4	12.4
Ni (ppm)	7.6	40	1.0	8.1	3.9	3.5
Cu + Fe (ppm)			0.8	3.5	0.2	0.2
Heptane insolubles (weight percent)	<0.006	<0.006				
Asphaltene fraction						
Specific gravity at 16 C (60 F)	1.104	1.140	1.083	1.120	1.120	1.086
Softening point (R&B), C (F)	120 (248)	177 (351)	77 (171)	119 (246)	107 (224)	134 (278)
Sulfur (weight percent)	3.25	3.8				
Heptane insolubles (weight percent)	20	48				
Metals rejection to asphaltene fraction (%)	98.5	81.0	96.6	98.2	97.1	96.5
Sulfur rejection to asphaltene fraction (%)	66	41				
Reference (Author)	Ditman	Ditman	Sinkar	Sinkar	Sinkar	Sinkar

TABLE 60. (Continued)

Crude Oil Type	Mideast	Mideast	Venezuelan	Kuwait	Kuwait
Residuum feedstock					
Specific gravity at 16 C (60 F)	1.031	1.014	1.002	1.030	1.030
Viscosity at 99 C (210 F), SUS[(a)]	14,200	3,270			
Conradson carbon residue (weight percent)	24.0	19.7	17.5	18.5	18.5
Sulfur (weight percent)			3.05	5.23	5.23
V (ppm)	110.0	89	550	106	106
Ni (ppm)	29.9	29.7	30	25	25
Cu + Fe (ppm)	13.7	7.5			
Heptane insolubles (weight percent)			8	9	9
Deasphalted oil product					
Yield (volume percent of feed)	45.6	54.8	75.1	63.6	83.1
Specific gravity at 16 C (60 F)	0.957	0.952	0.961	0.971	0.991
Viscosity at 99 C (210 F), SUS[(a)]	490	656	710	560	1,110
Conradson carbon residue (weight percent)	4.5	5.4	8.0	8.0	12.7
Sulfur (weight percent)			2.58	4.14	4.8
V (ppm)	0.7	4.0	59	10	23
Ni (ppm)	0.9	0.6	5	4	6
Cu + Fe (ppm)	0.8	0.8			
Heptane insolubles (weight percent)					
Asphaltene fraction					
Specific gravity at 16 C (60 F)	1.086	1.092	1.10	1.06	1.21
Softening point (R&B), C (F)	94 (201)	89 (193)			
Sulfur (weight percent)			4.1	6.7	7.2
Heptane insolubles (weight percent)					
Metals rejection to asphaltene fraction (%)	98.7	95.8	92.1	93.6	82.3
Sulfur rejection to asphaltene fraction (%)			39	52	27
Reference (Author)	Sinkar	Sinkar	Selvidge	Selvidge	Selvidge

(a) Saybolt universal seconds.

of a lower yield of product. For a given feedstock, a plot of metals removal (selectivity) versus yield can be developed. The relatively low product yields have been a drawback to further use of solvent deasphalting.

In solvent deasphalting the major selectivity is by molecular weight, with the lower molecular weight components being more soluble in the solvent. Molecules containing oxygen-bearing functional groups, such as the hydroxyl and carboxyl groups, are less soluble than similar molecules without such groups. A secondary selectivity is the preference for paraffinic molecules over aromatic molecules. Also, solvent deasphalting will dissolve and recover a hydrocarbon containing single rings connected by carbon chains, while rejecting a lower-boiling hydrocarbon containing a "chicken wire" structure of condensed rings.(236)

Although propane is the most common solvent for deasphalting, higher molecular weight paraffins can also be used. Deasphalting processes are available which use a light naphtha solvent (C_6-C_8).(239) With other variables fixed, increasing the molecular weight of the solvent increases the yield of deasphalted oil but decreases the quality of this product somewhat.

3.1.6 Stripping

Impurities present in oil in the form of dissolved gases can be removed by a stripping process, that is, contacting the oil with an inert gas stream. The two most common impurities which can be removed in this manner are H_2S and NH_3.

Gorodnov(240) has studied the stripping of H_2S from petroleum. An oil having a specific gravity of 0.894 and a viscosity of 47.5 centipoise at 20 C and containing 550 to 650 mg H_2S/liter was contacted with inert gas in a countercurrent scrubber. The scrubbing temperature was varied from 14 to 68 C and the gas flow rate from 4.7 to 12.5 volumes/volume of oil/hour. The maximum degree of H_2S removal achieved was 99.0 percent.

Stripping of oil with inert gases is not practiced as a distinct operation in refineries because the H_2S and NH_3 are readily separated from the oil during the normal distillation operations. The technique would be useful only if crude oil were to be used directly as a fuel without prior distillation, and only sulfur and nitrogen present as H_2S and NH_3, respectively, would be removed. Distilled fuels contain only very small quantities of H_2S and NH_3.

3.2 Hydrotreating

3.2.1 Introduction

Hydrotreating processes are used extensively to remove sulfur and nitrogen from petroleum fractions. In these processes, the petroleum feedstock and a hydrogen-rich gas are passed through a catalytic reactor at an elevated temperature and pressure. In this reactor, sulfur and nitrogen compounds in the feedstock are converted to H_2S and NH_3, respectively. The resulting gas and liquid phases are separated, and the gas is scrubbed to remove the H_2S and NH_3 and is recycled to the reactor. A typical flow sheet is shown in Figure 37.(241)

A wide range of possible feedstocks and operating conditions can be used. The terms "hydrotreating" and "hydrorefining" are often used for the processes employing relatively mild conditions* and removing only traces of sulfur and nitrogen, usually from light fractions such as naphtha. The term "hydrodesulfurization" is used for the processes employing more severe conditions to remove large quantities of sulfur and nitrogen from heavier fractions such as "gas oils" and residua. To clarify the terminology, the following is a list of petroleum fractions that can be hydrotreated (in the general sense of the term).

Fraction	Approximate Boiling Range, C (F)
Naphtha	15-220 (60-430)
Atmospheric gas oil	220-340 (430-650)
Vacuum gas oil	340-565 (650-1050)
Atmospheric residuum	340+ (650+)
Vacuum residuum	565+ (1050+)

The heavier the feedstock the less advanced is the technology for hydrotreating and the more expensive is the operation. Hydrodesulfurization

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[*] Specific temperatures and pressures are not available because the processes are proprietary. However, hydrogen consumption data are available and do indicate the severity of the hydrotreating operations. Hydrogen consumptions are generally less than 200 scf/bbl feed for light fractions such as naphtha and are greater than this value for gas oils and residua.

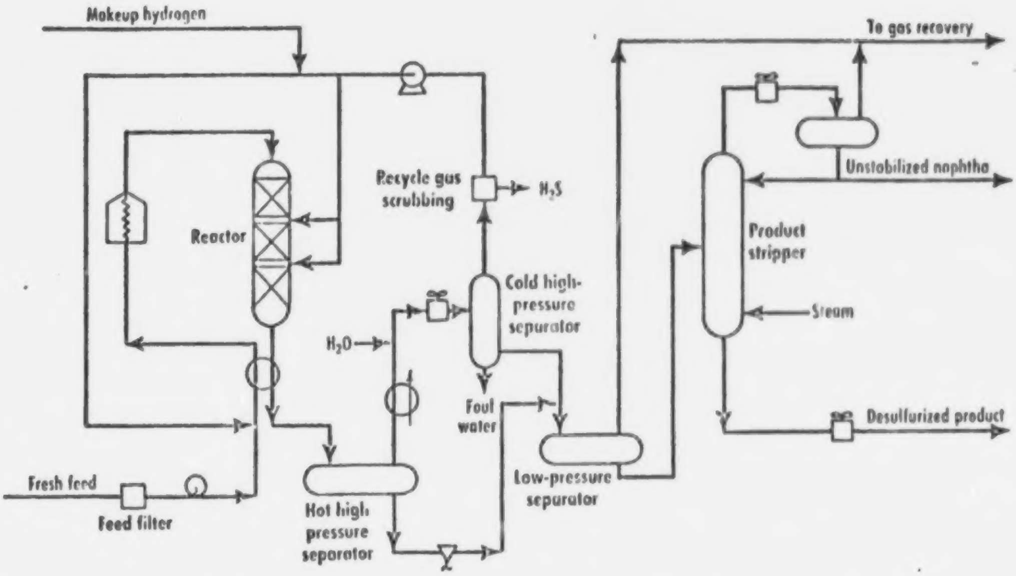

Makeup hydrogen
To gas recovery
Recycle gas scrubbing
H_2S
Reactor
Unstabilized naphtha
Product stripper
Cold high-pressure separator
Steam
H_2O
Foul water
Desulfurized product
Fresh feed
Feed filter
Hot high pressure separator
Low-pressure separator

FIGURE 37. FLOW SHEET FOR CHEVRON ISOMAX HYDRODESULFURIZATION PROCESS(241)

of atmospheric and vacuum residua has only recently become a commercially feasible option for most crude oils, and it is still not considered feasible for very high metals crudes such as some of the Venezuelan crudes, the residua of which contain over 400 ppm of V + Ni.

Even within the classifications of process types listed above, a relatively large number of individual processes are used commercially or offered for commercial use. This is illustrated by the list of commercial hydrodesulfurization processes presented in Table 61.(241) The primary differences among the various processes of a given type are in the details of the catalysts used, although some differences also exist in the reaction conditions and process configurations. Most of the processes use fixed-bed reactors, although the H-Oil process uses an ebullating bed.

The primary purpose of hydrotreating is to remove sulfur, and this is what it does best. Nitrogen is more difficult to remove and hence requires more severe conditions. Metals are only partially removed.

3.2.2 Catalysts

The catalysts most commonly applied in hydrodesulfurization are derived from alumina-supported oxides of cobalt and molybdenum, which are usually sulfided in operation. Catalysts of this type are commonly referred to as cobalt molybdate. Practical catalysts may contain as much as 10 to 20 percent of these metals, though lower metal contents are probably more common. A number of related compositions have been applied, including, for example, nickel and tungsten. In contrast to the supported platinum and platinum-alloy catalysts used in reforming, the hydrodesulfurization catalysts have hydrogenation activity in the presence of high concentrations of sulfur compounds.

The catalysts are used as porous pellets or extrudates, typically 1.6 to 3.2 x 10^{-3} meter. The particle size and pore geometry have an important influence on process design (especially for the heaviest feeds) since intraparticle mass transport has a significant influence on reaction rates.(242)

TABLE 61. COMMERCIAL HYDRODESULFURIZATION PROCESSES[242]

Company	Process Name	Feedstocks[a]	Desulfurization Capability[b]
Chevron Research Company	Isomax VGO	VGO	90-95%
	Isomax RDS	AR	~85%
	Isomax VRDS	VR	>70%
Cities Service/HRI	H-Oil	VGO, AR, VR	
Exxon Research and Engineering Company	Go-Fining	VGO	90%
	ResidFining	AR	~74%
Gulf Research and Development Company	GulFining	VGO	80-95%
	Types I & II	AR	~75%
	Type III	AR	~88%
Institut Francais du Petrole	IFP HDS	VGO	~90%
	IFP HDS	AR	~88%
Standard Oil (Indiana)	UltraFining	VGO	80-90+%
	UltraFining	AR, VR	75-90%
Universal Oil Products	RCD Isomax	AR	~87%

(a) VGO - vacuum gas oil (650-1050 F); AR - atmospheric residuum (650+ F); VR - vacuum residuum (1050+ F).

(b) For residua, examples given had V + Ni < 210 weight ppm.

3.2.3 Reaction Mechanisms

The reaction mechanisms and kinetics of hydrodesulfurization have been reviewed by Schuit.(242) The desired reactions are hydrogenolysis reactions which result in cleavage of a C-S bond. For example,

$$R\text{-}SH + H_2 \dashrightarrow R\text{-}H + H_2S.$$

These reactions are virtually irreversible at the temperatures and pressures ordinarily used, which are roughly 330 to 480 C (630 to 900 F) and up to 2×10^7 N/m^2 (3000 psi). The hydrodesulfurization reactions are exothermic with heats of reaction of 5 to 9×10^4 joules/g-mole H_2 consumed (60 to 110 Btu/scf H_2 consumed).

The general order of reactivity of sulfur compound types in hydrodesulfurization is as follows:

Thiols (mercaptans)	Most reactive
Disulfides	
Sulfides	
Thiophenes	
Benzothiophenes	
Dibenzothiophenes	
Benzonaphthothiophenes	Least reactive

The reaction networks prevailing in catalytic hydrodesulfurization are known for only a few reactants, and results are not easily generalized. Compounds such as thiophene and benzothiophene have been used as models in various studies. For thiophene, the desulfurization (breaking of C-S bonds) occurs before the hydrogenation of the double bonds. In contrast, benzothiophenes are evidently hydrogenated first and then desulfurized. The reactivities of compounds within the class of substituted benzothiophenes vary significantly, indicating the difficulty of generalizing results on the basis of a small number of compound classes.(242)

3.2.4 Kinetics

The hydrodesulfurization reactions for many sulfur compounds, including dibenzothiophene, over a wide range of conditions are first order with respect to both the reactant concentration and hydrogen partial pressure. The reactivity of sulfur compounds in hydrodesulfurization reactions decreases as the molecular weight of the compound increases. The reactions are inhibited by the product H_2S and by strongly adsorbed hydrocarbons.

3.2.5 Side Reactions

Three types of side reactions occur in hydrotreating. The first is hydrogenation of hydrocarbons. A considerable amount of saturation of naphthenic and aromatic hydrocarbons occurs, and as a result the hydrogen consumption far exceeds the amount required to react with the sulfur and nitrogen removed. The more severe the operating conditions the more hydrogenation of hydrocarbons occurs. This is illustrated by the data shown in Figure 38.(243) To achieve 76 percent desulfurization of the feedstock involved, only 130 scf/bbl of hydrogen is stoichiometrically required to convert the sulfur to H_2S, and an equal amount is needed to replace the sulfur in the parent molecules. This "theoretical" hydrogen consumption of 260 scf/bbl was approached experimentally only at very low pressures. For this feedstock, at the normal operating pressures, more than 50 percent of the hydrogen consumed during hydrodesulfurization is used to hydrogenate the feedstock. The hydrogen consumption is a major cost item of a hydrotreating process.

The second type of side reaction is conversion, that is, cracking of the feedstock molecules to produce smaller, lower boiling species. These light products often must be fractionated out of the product. There is a process known as hydrocracking which involves reaction of oil and hydrogen over a catalyst for the purpose of cracking the feedstock, but this is not considered here because it is not a contaminant-removal process. However, it should be mentioned that a hydrocracking unit normally includes a hydrotreating reactor as its first stage to remove sulfur and nitrogen from the feedstock. The actual hydrocracking catalyst, which usually contains noble metals, is used in the second and third stages (some processes use three stages).

The third type of side reaction is coking, which is common to virtually all hydrocarbon reaction processes. Coke is deposited on the

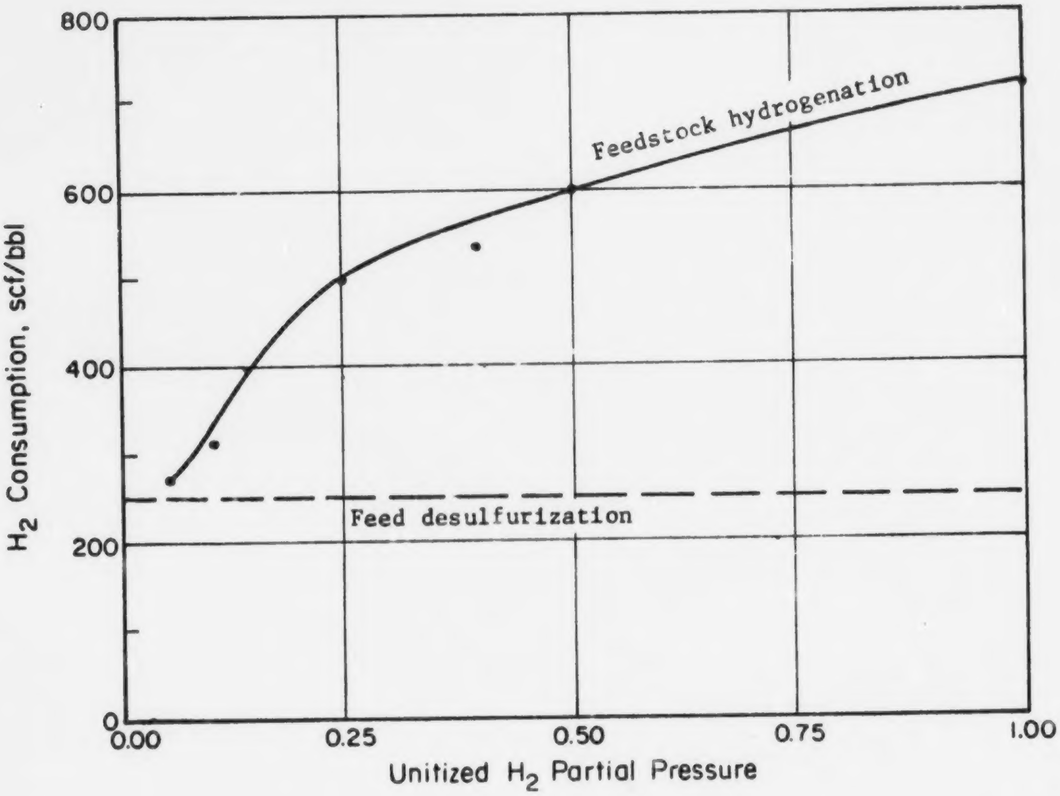


FIGURE 38. TYPICAL HYDROGEN CONSUMPTION IN HYDRODESULFURIZATION(243)

catalyst through the decomposition and polymerization of heavy asphaltic molecules. The deposition of both coke and metals reduces the activity of the catalyst. However, unlike the metals, the coke can be burned off the catalyst if the economics justify a regeneration procedure.

3.2.6 Sulfur Removal

The degree of sulfur removal that can be obtained at practical (economical) hydrotreating conditions depends primarily on feedstock characteristics such as boiling range, sulfur content, and metals content. Light naphtha feeds can be desulfurized to a few ppm of sulfur, and this is regularly done in preparing feeds for catalytic reforming. For gas oils, sulfur removals of 90 to 95 percent are common, this normally corresponding to 0.2 to 0.3 weight percent sulfur in the product. For low metals residua, sulfur removals of 85 to 90 percent are common, and at this level, 0.5 weight percent sulfur fuel oils can be made. For high metals residua (>200 ppm V + Ni), the commercial experience is rather limited but the sulfur removal is often limited to about 75 percent. Some typical data on the hydrodesulfurization of gas oils and residua are shown in Table 62.(241)

3.2.7 Nitrogen Removal

The reactions of nitrogen compounds during hydrotreating of a gas-oil fraction was studied by Aboul-Gheit.(244) The feedstock was a 200 to 400 C (390 to 750 F) fraction from a Middle East crude oil. A tungsten nickel sulfide on alumina catalyst was used. In this study the nitrogen compounds were classified into three groups:

Strongly basic nitrogen - alkylamines, alkylpyridines, anilines, quinolines, phenanthridines, and other compounds containing two nitrogen atoms, one of which is titratable (e.g., phenazines and pyrazines)

Weakly basic nitrogen - amides, imides, lactams, carbamates, pyroles, and indoles

Nonbasic nitrogen - carbazoles, nitriles, and nonbasic nitrogen in the compounds containing two nitrogen atoms (one of which is basic).

TABLE 62. TYPICAL DATA ON HYDRODESULFURIZATION OF GAS OILS AND RESIDUA(241)

Process	Isomax	Go-Fining	Resid. Fining	Gulfining	Gulf Type III	IFP	IFP
Feedstock:							
Crude Oil Type	Arabian Light	Kuwait	Kuwait		Kuwait		Kuwait
Fraction	Atm Residuum	Vac Gas Oil	Atm Residuum	Vac Gas Oil	Atm Residuum	Vac Gas Oil	Residuum
Boiling Range, C(F)	340+(650+)	340-565(650-1050)	340+(650+)	340-565(650-1050)	340+(650+)	294-400+(562-750+)	300+(572+)
Specific Gravity	0.951	0.921	0.957	0.941	0.955	0.898	0.963
Sulfur, wt. %	3.1	3.05	3.8	2.7	3.8	2.5	4.1
Nitrogen, wt. %	0.19						0.25
V + Ni, ppm	38		55		60		63
Product:							
Boiling Range, C(F)	340+(650+)	204+(400+)	204+(400+)	340+(650+)	340+(650+)		204+(400+)
Yield, vol. % of feed	93.0	99.0	100.7	94.0	90.9	98.4	99.5
Specific Gravity	0.922		0.918	0.91	0.922	0.876	0.905
Sulfur, wt. %	0.5	0.3	0.5	0.2	0.5	0.25	0.5
Nitrogen, wt. %	0.09						
V + Ni, ppm							17
Sulfur Removal, %	86	90	87	93	87	90	89
Chemical H_2 Consumption, scf/bbl		280	640	425	815	232	760
Catalyst Life, months							9

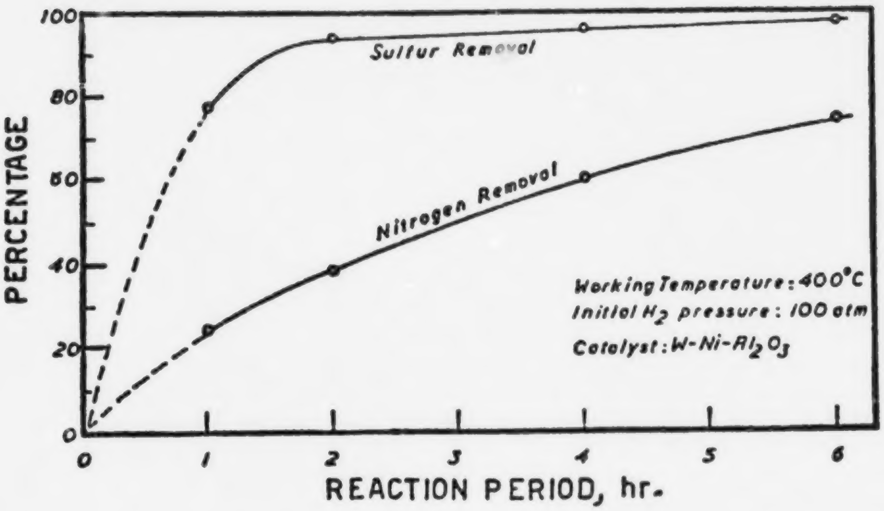
The feedstock contained 2,175 ppm total nitrogen, and the breakdown by types was 8.4 percent strongly basic, 11.4 percent weakly basic, and 80.2 percent nonbasic.

Some data from this study are shown in Figure 39. The top plot illustrates the point, which was already mentioned, that nitrogen is more difficult to remove by hydrotreating than is sulfur. The bottom plot shows that the ease of removal of the nitrogen compounds increases as the basicity of the compounds increases.

Distillation of the feedstock and subsequent analysis showed that the 350 to 400 C fraction comprised 30 weight percent of the feed but contained 50 percent of the nitrogen. The nitrogen compounds present in this fraction were the most converted, which is due partially to the occurrence of easily denitrogenated nonrefractory types and partially to degradation to other nitrogen compounds present in the lower boiling fractions. The degradation of the higher-boiling nitrogen compounds was evidenced by an increase in the percentage of the lower boiling fractions due to a decrease in the higher boiling fractions upon hydrotreating.(244)

3.2.8 Metals Removal

The various hydrotreating catalysts differ in the extent to which they remove metals from the oil. This is illustrated in Figure 40(243-246) by typical plots of demetallization/desulfurization ratio versus H_2 partial pressure and of metals removal versus sulfur removal. The organometallic compounds react to give inorganic products, which can plug the pores of the catalyst or, ultimately, plug a fixed bed of catalyst particles. Guard chambers are often used to trap the metals ahead of the desulfurization reactors.(246) When metals deposit on the catalyst, they reduce the activity of the catalyst, thereby decreasing the catalyst life. The catalysts that pick up more metals may be credited with producing a cleaner fuel product but will have a shorter life.



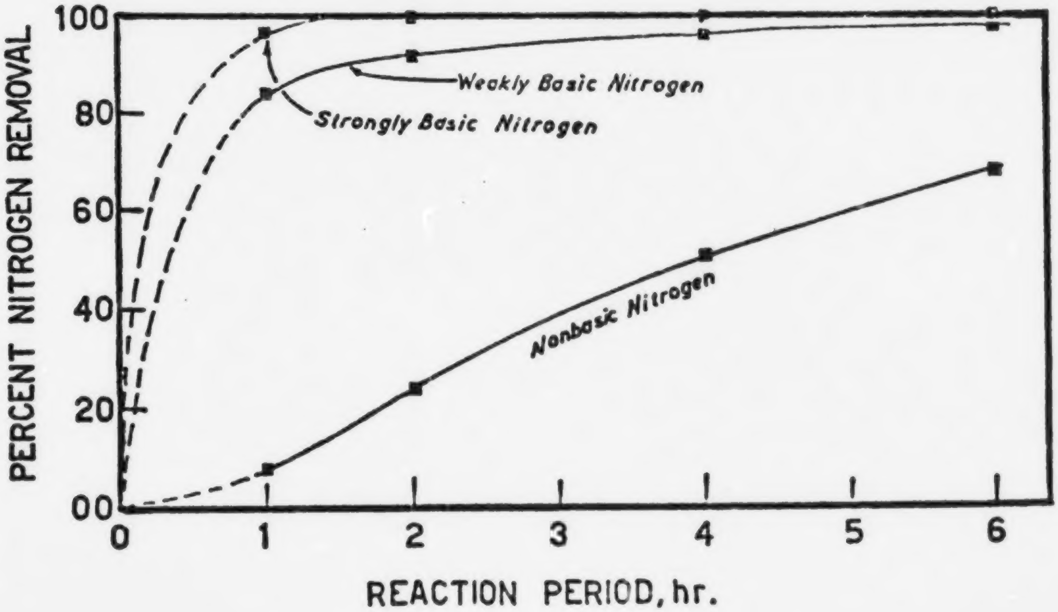
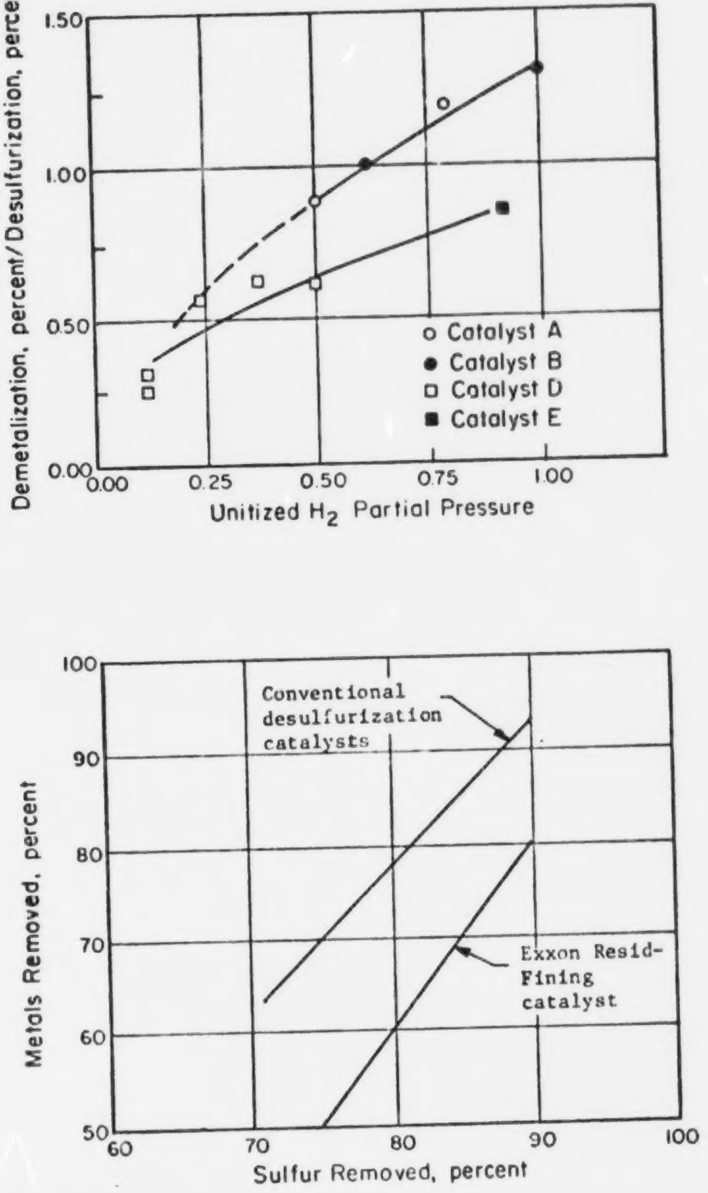


FIGURE 39. SULFUR AND NITROGEN REMOVAL IN HYDROTREATING OF GAS OIL(244)



Feedstock: Atmospheric residuum.

FIGURE 40. RELATIONSHIPS OF METALS REMOVAL TO SULFUR REMOVAL IN HYDRODESULFURIZATION(243-246)

3.2.9 Application to Petroleum Coke

Noncatalytic hydrotreating can be used to remove sulfur from petroleum coke. This has been studied by Sef(247) using coke prepared from a Yugoslavian (Klostar) crude oil. The coke samples contained 1.84 to 2.01 weight percent sulfur. Mixtures of hydrogen and nitrogen were passed through a fixed bed of finely ground coke particles. The results of these experiments are shown in Figure 41.

The highest sulfur removal obtained in these experiments was 93.6 percent. The plots in Figure 41 show that the sulfur removal increases with increasing pressure (H_2 partial pressure), with increasing space velocity of hydrogen, and with decreasing coke particle size. As the sulfur removal increases, the yield of coke product decreases. At 90 percent sulfur removal, the yield is about 79 percent. The balance of the coke is gasified during the treatment. Although no external catalyst is used in this treatment, metals in the coke, particularly nickel, probably have a catalytic effect on the reactions.

3.3 Chemical Refining

3.3.1 Sulfuric Acid Treatment

Treatment of petroleum fractions with sulfuric acid (H_2SO_4) has been used commercially for many years. One objective of this treatment is to remove sulfur and nitrogen, which is within the scope of this study. Other objectives include the removal of various hydrocarbon types to improve the quality of products. The rate of action of sulfuric acid on the species which it can remove (excluding sulfur compounds) is generally:

Nitrogen compounds such as amines, amides, and amino acids	Greatest
Asphaltic or resinous substances	
Olefins	
Aromatics	
Naphthenic acids	Least.(248)

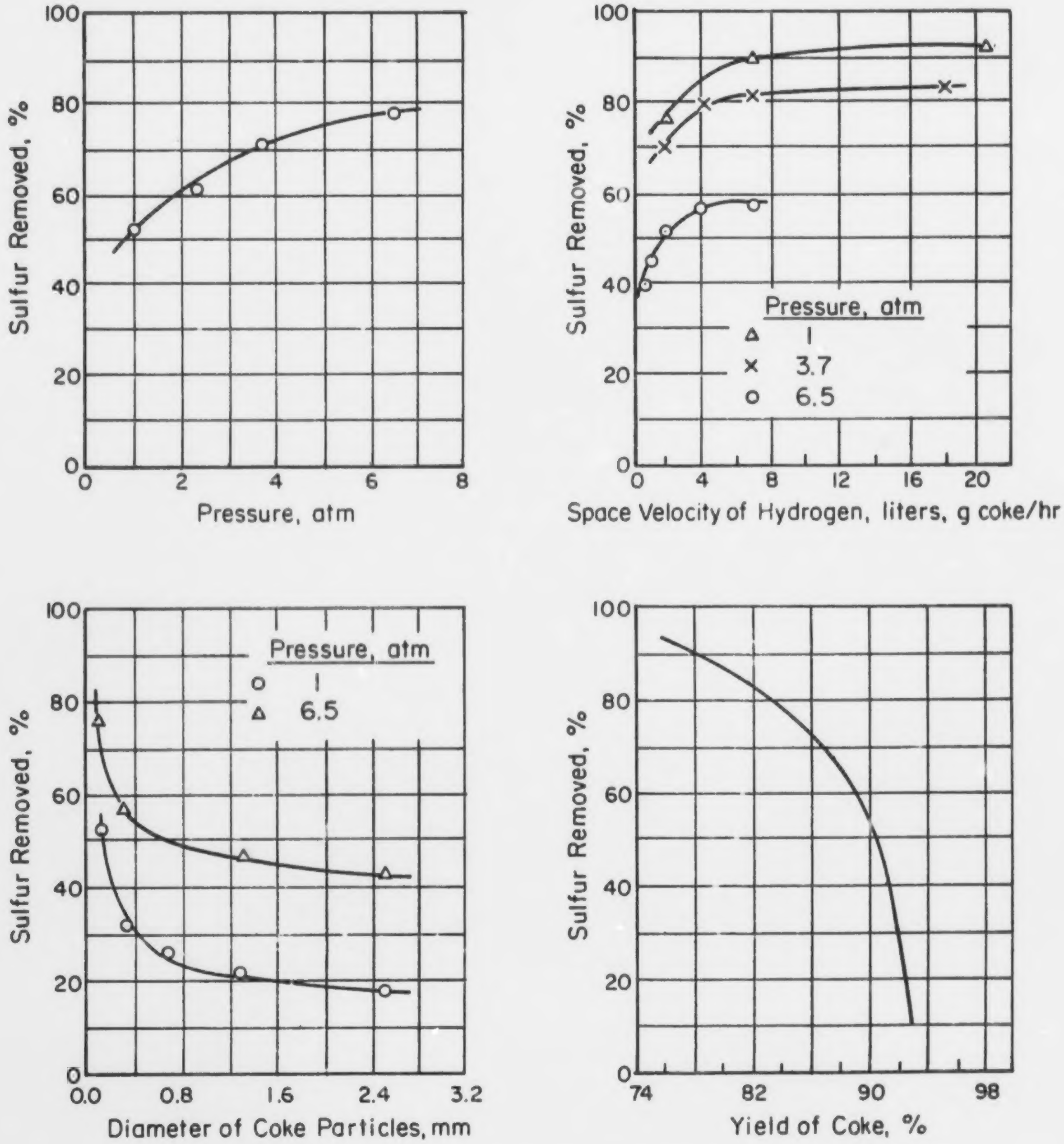


FIGURE 41. EFFECTS OF VARIABLES ON DESULFURIZATION OF PETROLEUM COKE BY NONCATALYTIC HYDROTREATING(247)

The ability of sulfuric acid to promote reactions of olefinic hydrocarbons is shown by the fact that it is used as a catalyst in the alkylation and polymerization processes of refineries.

A study of the effectiveness of sulfuric acid in removing sulfur species from oil was conducted by Wood.(233) In this study, solutions of various single, pure organic sulfur compounds in naphtha were treated with sulfuric acid of three different strengths, fuming, 66 Bé (93 weight percent H_2SO_4), and 53 Bé (67 weight percent). The descriptions of the removal efficiencies given by Wood are presented in Table 63. The results show that free sulfur and carbon disulfide were not affected by the fuming, less readily by the 66 Bé, and very sparingly, if at all, by the 53 Bé acid. Several other strenghts of acid were tried on the mercaptan solution: the 63 Bé acid removed about 20 percent of the mercaptan; 44 Bé and 24 Bé acid did not affect the mercaptan. These results can be readily explained on the basis of the oxidizing and solvent action of sulfuric acid. Fuming sulfuric acid, being the best oxidizing and dissolving agent, readily converts the mercaptan to the corresponding disulfide and dissolved it as such. The 66 Bé acid is not as strong an oxidizing agent, but when used in sufficient quantity will convert and remove the mercaptan in the form of the disulfide. In the oxidation of the mercaptan to the disulfide, the alkyl acid thiosulfate and the alkyl dithiosulfate are perhaps formed as intermediate products. The quantity of acid used must be sufficient to carry the oxidation through these intermediate steps and then dissolve the resulting disulfide. As the acid become more and more dilute, the oxidizing and dissolving power gradually decreases. This fact probably accounts for the ineffectiveness of the 53 Bé acid.

The fuming and 66 Bé acids oxidize hydrogen sulfide to free sulfur, in which form it is left in the naphtha. The effect of the 53 Bé acid could not be accurately checked because the acid was apparently too dilute to oxidize the hydrogen sulfide.

Dimethyl sulfate, methyl p-toluenesulfonate, n-butyl sulfide, n-propyl disulfide, thiophene, diphenyl sulfoxide, and n-butyl sulfone were removed by the fuming and 66 Bé acids. The thiophene was removed as thiophenesulfonic acid, while the others were dissolved apparently unchanged. These results would indicate that while concentrated sulfuric acid is a

TABLE 63. DEGREE OF REMOVAL OF SULFUR SPECIES FROM OIL BY SULFURIC ACID TREATMENT(233)

Species Contained in Naphtha Solution	Strength of H_2SO_4 Used		
	Fuming	66 Bé	53 Bé
Free sulfur	None	None	None
Isoamyl mercaptan	Removes as disulfides	Removes as disulfides	None
Hydrogen sulfide	Forms naphtha solution of free sulfur	Forms naphtha solution of free sulfur	No oxidation to free sulfur
Dimethyl sulfate	Removes readily	Removes readily	Removes fairly well
Methyl-p-toluene-sulfonate	Removes readily	Removes fairly well	None
Carbon disulfide	None	None	None
n-Butyl sulfide	Removes readily	Removes	None
n-Propyl disulfide	Removes readily	Removes fairly well	None
Thiophene	Removes as thiophene-sulfonic acid	Removes as thiophene-sulfonic acid	None
Diphenyl sulfoxide	Removes readily	Removes	Removes fairly well
n-Butyl sulfone	Removes readily	Removes	Removes fairly well
Percent of total sulfur removed in two experiments	79	53,76	13,16

sufficiently strong oxidizing agent to convert the mercaptan to the disulfide and to convert hydrogen sulfide to free sulfur, it is not strong enough to oxidize naphtha solutions of any of the alkyl sulfides to the sulfoxide or to the sulfone. The 53 Bé acid removed most of the alkyl sulfate, sulfoxide, and sulfone, but had little effect on the others.

These results indicate that the desulfurizing power of sulfuric acid is a function of its concentration. The dilute acid is not an effective desulfurizing agent. It also appears that a cracked distillate containing appreciable quantities of hydrogen sulfide should be subjected to an alkali wash prior to an acid treatment; otherwise, free sulfur, a corrosive substance, is introduced into the naphtha. Free sulfur may be removed from a distillate by redistillation or by treatment with an alkaline lead mercaptide solution. The prior treatment with alkali would also remove some of the mercaptan, which would be an additional advantage for the acid treatment.(233)

Chertkov(249) has studied the extraction of sulfur from a petroleum distillate with sulfuric acid. A 150 to 325 C (302 to 617 F) fraction of a Russian crude oil (Arlansk) was used as the feedstock. This fraction contained 1.57 weight percent sulfur. The best conditions for the initial extraction were found to be an acid concentration of 86 weight percent and an acid/oil ratio of 1/5 to 1/10 at ambient temperature and pressure. Further extractions of the product with 86 percent acid did not result in any additional sulfur removal. For a two-step extraction, use of 91 percent acid for the second extraction was recommended. Results based on this procedure are shown in Table 64. About 71 percent of the total sulfur was removed. The effectiveness of the acid in removing sulfides is in agreement with the work of Wood.(233) Chertkov speculated that the mechanism for sulfide removal may involve the formation of weak sulfonium complexes which are soluble in the acid. He noted that thiophenes do not dissolve in aqueous solutions of sulfuric acid since their ability for protonization reactions is insufficient.

The fact that sulfuric acid reacts with and promotes reactions of hydrocarbons is a drawback to its use as an agent for removing sulfur and nitrogen from oil. The hydrocarbon reactions increase the quantity of acid required and decrease the yield of fuel product. One source(250)

TABLE 64. RESULTS OF TWO-STAGE EXTRACTION OF PETROLEUM DISTILLATE WITH SULFURIC ACID(249)

Feedstock: 150-325 C (302-617 F) Fraction of Arlansk Crude Oil

Acid Strengths: 86 wt % H_2SO_4 for first extraction,
91 wt % for second extraction

Feedstock -	
Specific gravity at 20 C	0.820
Sulfur (wt %)	
Total	1.57
Sulfide	1.02
% of Sulfur present as Sulfide	65
Product -	
Yield, weight % of feed	90.85
Sulfur (wt %)	
Total	0.50
Sulfide	0.06
% of Sulfur present as Sulfide	12
% Removal of all Sulfur	71
% Removal of Sulfide only	95

states that for sulfur removal, "Sulfuric acid treatment is not a satisfactory process because it dissolves much of the product as well as the sulfur compounds and polymerizes olefin hydrocarbons". The extent to which this is true depends on the nature of the feedstock. Sulfuric acid treating is best for paraffinic feeds but much less desirable for feeds which contain a lot of aromatic compounds, such as residual fuel oil.

3.3.2 Other Acid Treatments

Like sulfuric acid, hydrofluoric acid (HF) is used commercially as a catalyst for alkylation processes. One would, therefore, expect HF to be similar to H_2SO_4 in its abilities to extract sulfur and nitrogen compounds from oil and to promote reactions of certain types of hydrocarbons. HF is claimed to be more effective than H_2SO_4 for sulfur removal.* HF is a weaker acid than H_2SO_4 but presents some greater safety hazards.

Kotova(251) has studied the extraction of vanadium from crude oils and petroleum products using aqueous solutions of sulfonic acids. Three acids were found to be effective -- n-toluenesulfonic, o-sulfonobenezoic, and sulfanilic. It was found to be easier to extract vanadium from crude oils and petroleum products which did not contain a vanadium-porphyrin complex.

The ability of aromatic sulfo acids to extract nitrogen compounds from hydrocarbon fractions has been shown in Tokareva.(252)

The ability of acids to decompose metalloporphyrin compounds has been studied by Don and Yen.(253) Three acids were studied -- hydrochloric, sulfuric, and methanesulfonic. Two pure porphyrin compounds were used -- copper meso-tetraphenylporphyrin (Cu-TPP) and copper etioporphyrin I (Cu-Etio I). All reactions were carried out at 24 C (75 F) in a glacial acetic acid medium.

Cu-Etio I was found to be more susceptible to demetallization than Cu-TPP. In a 0.4 N acid medium, Cu-Etio I underwent an appreciable conversion in 2.5 hours, whereas Cu-TPP remained essentially unchanged. However, work was concentrated on Cu-TPP because of its greater availability.

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* This statement was included in the first edition of the Encyclopedia of Chemical Technology (Reference 249) but not in the second edition. No supporting information has been found.

Hydrochloric acid proved to be inferior to the other two acids used. Not only was its solubility in acetic acid low (continuous bubbling of HCl gas through glacial HOAc for 5 hours gave a solution of acid strength of 0.951 N), offering a limited acid strength range, but also it was not stable in solution, posing difficulty in controlling the acid strength. Sulfuric acid provided a limited range owing to its immiscibility with hydrocarbons at an acid concentration above 4N. Methanesulfonic acid offered the widest workable range, was easiest to handle, and proved to be the most useful demetallization reagent. Plots of the data indicated that at acid concentrations less than about 4.4 N, sulfuric acid is a more efficient demetallization reagent than methane-sulfonic acid, whereas the reverse is true for concentrations greater than 4.4 N.

It should be noted that the decomposition of metal-containing compounds does not constitute metals removal in itself, but presumably the decomposition step could be followed by a washing to remove the freed metals.

3.3.3 Caustic Alkali Treatment

Treatment of petroleum fractions with aqueous solutions of caustic (NaOH or KOH) has been used commercially to remove mercaptans. This treatment does not remove the more complex sulfur species. Wood(233) has studied the effectiveness of NaOH in removing sulfur species from oil. In this study, solutions of various single, pure sulfur compounds in naphtha were treated with NaOH solutions of two strengths, 10 percent and 0.05 percent The descriptions of the removal efficiencies given by Wood are presented in Table 65. Only the mercaptan, H_2S, and the sulfate were removed.

The commercial caustic washing processes include the Shell Solutizer, Atlantic Unisol, and Pure Oil Mercapsol processes.(248,254) These processes use, in addition to the caustic, certain solubility promoters such as salts of isobutyric acid, alkyl phenols, methanol, cresols, and naphthenic acids. The Unisol process uses methanol at the center of a packed treating column and caustic soda throughout the entire lengt of

TABLE 65. DEGREE OF REMOVAL OF SULFUR SPECIES FROM OIL BY SODIUM HYDROXIDE TREATMENT(233)

Species Contained in Naphtha Solution	Degree of Removal[a]
Free sulfur	None
Isoamyl mercaptan	Removes partially as sodium mercaptides
Hydrogen sulfide	Removes as NaS
Dimethyl sulfate	Removes as Na_2SO_4
Methyl p-toluene-sulfonate	None
Carbon dioxide	None
n-Butyl sulfide	None
n-Propyl disulfide	None
Thiophene	None
Diphenyl sulfoxide	None
n-Butyl sulfone	None

(a) Sulfur removals in two experiments were

31,41 percent of isoamyl mercaptan
100 percent of hydrogen sulfide
25,100 percent of dimethyl sulfate
8,12 percent of total sulfur.

the column. Small amounts of methanol are lost with the oil, and the methanol must be distilled after it (and the mercaptans) has been stripped from the caustic solution. The Mercapsol process uses a mixture of cresols and naphthenic acids which can be repeatedly regenerated. Caustic solutions having concentrations of 5 to 15 percent are normally used in these processes.(248)

A flow sheet of the Solutizer process is presented in Figure 42. The steps in the process are caustic washing, solutizer washing to dissolve mercaptans, and stripping of the solutizer solution by means of steam. Contact is effected by means of a countercurrent tower packed with carbon Raschig rings, and the process is completely continuous. It may be applied for the sweetening of any type of distillate including cracked, reformed, or poly distillates. The ratio of solution to gasoline in commercial plants ranges from 0.1 to 0.2. The equivalent of three theoretical plates is used in the extraction column and ten theoretical plates in the regenerator.(248)

In caustic washing, the ease with which mercaptans are removed from the oil decreases with increasing molecular weight of the mercaptan. This is shown in Figure 43.

Although most of the experience in caustic treatment of petroleum has involved aqueous caustic solutions, there are some data on higher temperature treatments with molten caustic. A patent issued to Murphy(255) deals with the desulfurization of petroleum, coke, coal, or char by treating with an alkali metal hydroxide, oxide, carbide, carbonate, or hydride at 260 to 450 C (500 to 850 F), i.e., above the melting point of the alkali metal used. A fluidized-bed system with intermittent introduction of steam and a final water wash is suggested. In an example given, a residuum containing 3.2 weight percent sulfur was preheated to 177 C (350 F) and then injected into molten NaOH at 260 to 274 C (500 to 525 F), thus causing about 75 percent of the oil to vaporize. The liquid oil phase was decanted, cooled, and water washed, after which it contained 1.5 weight percent sulfur. The vapor phase oil product was condensed and then washed with NaOH and water, after which it contained 0.9 weight percent sulfur. In this case, the sulfur removal was about 67 percent. The patent claims only 30 to 50 percent sulfur removal.

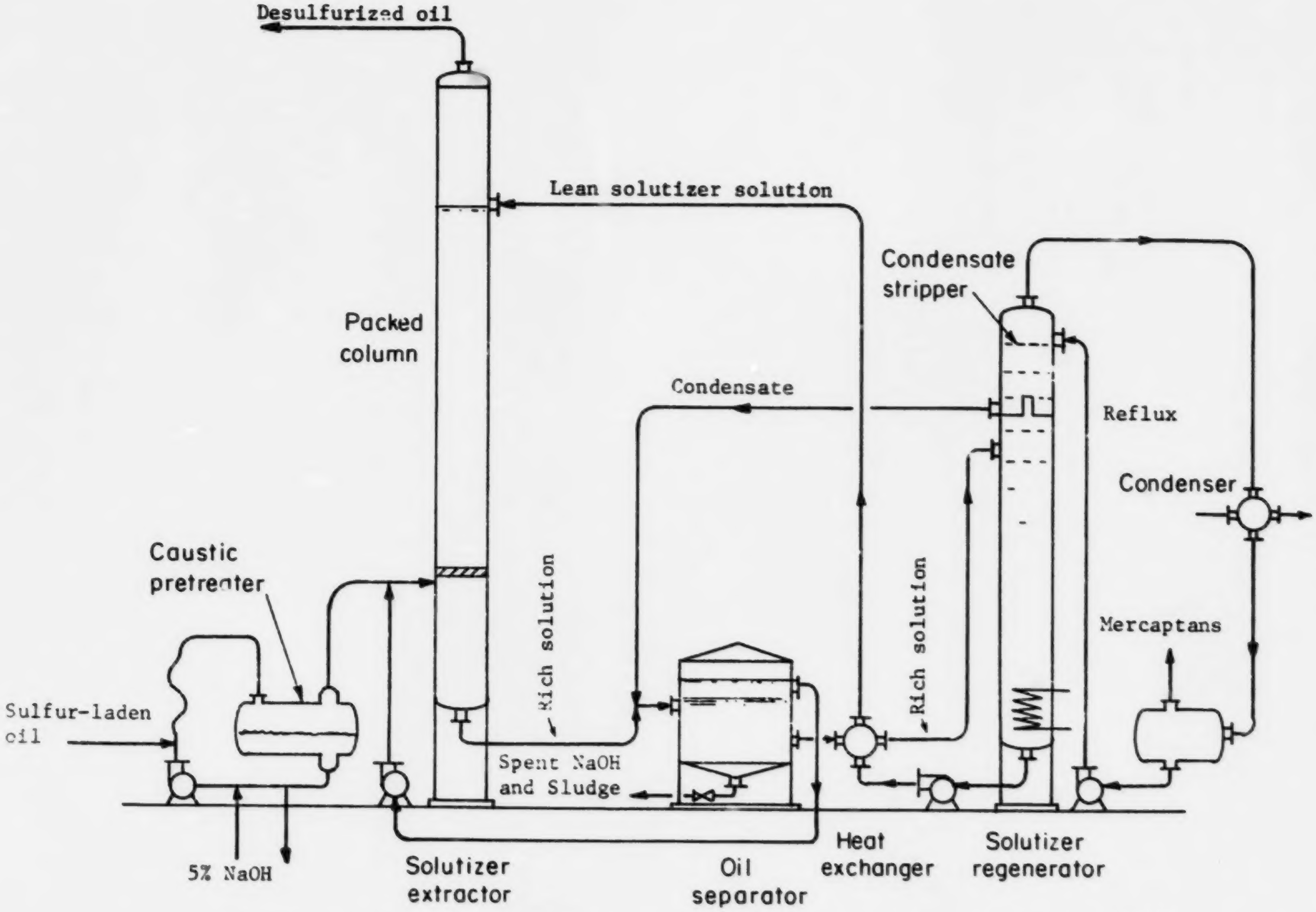

Desulfurized oil
Packed column
Lean solutizer solution
Condensate stripper
Condensate
Reflux
Condenser
Caustic pretreater
Rich solution
Rich solution
Mercaptans
Sulfur-laden oil
Spent NaOH and Sludge
5% NaOH
Solutizer extractor
Oil separator
Heat exchanger
Solutizer regenerator

FIGURE 42. FLOW SHEET FOR SHELL SOLUTIZER PROCESS FOR CAUSTIC TREATMENT(248)

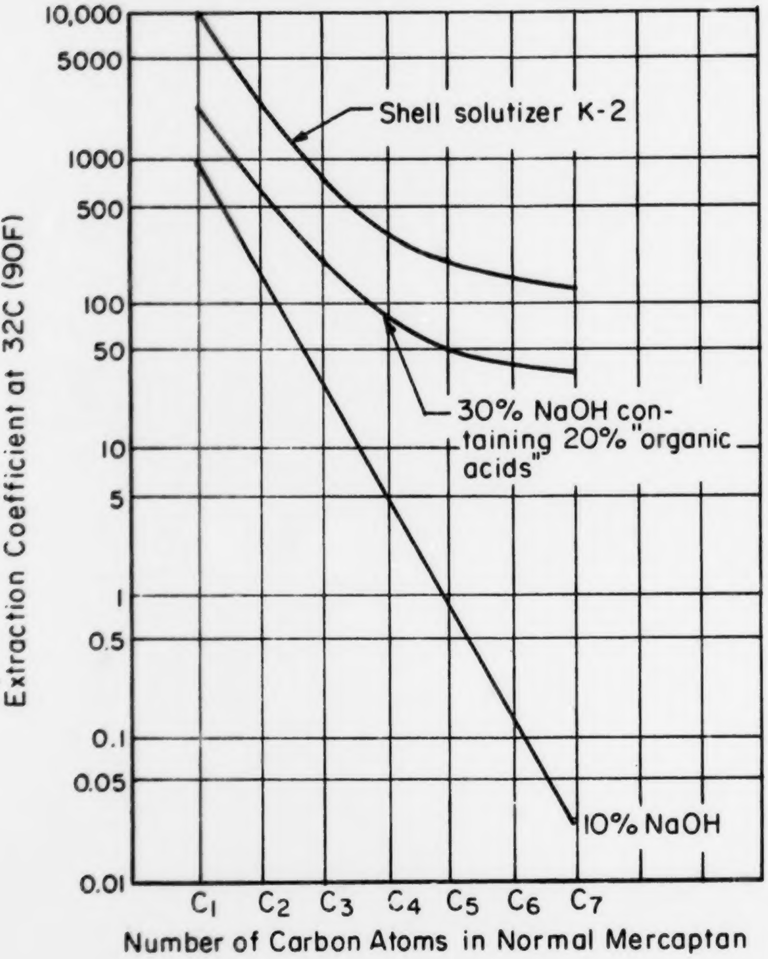


FIGURE 43. EXTRACTION COEFFICIENT FOR REMOVING MERCAPTANS FROM GASOLINE BY CAUSTIC WASHING(248)

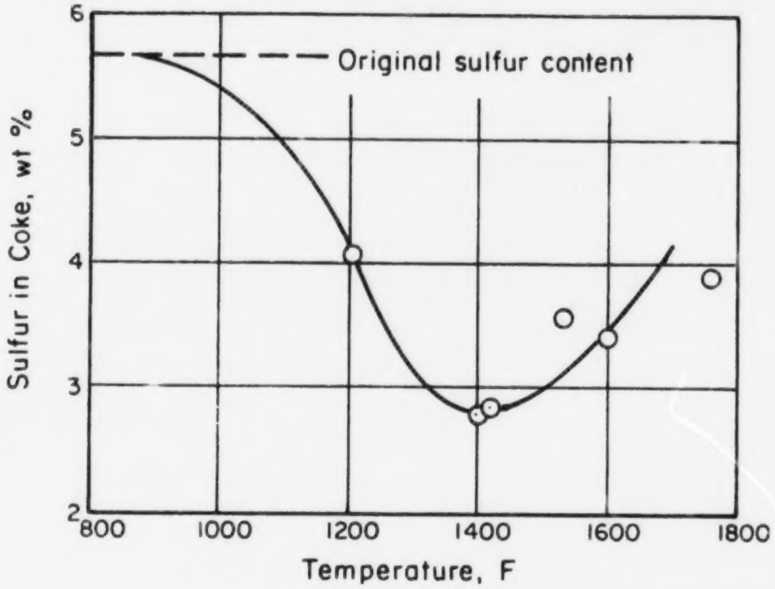
A patent has been issued to Hutchings(256) on the desulfurization of petroleum coke by treatment with molten alkali metal hydroxides, particularly those of sodium, potassium, and lithium. The examples given deal with the treatment with NaOH of a petroleum coke containing 2.88 weight percent sulfur. Treatment of the coke with an equal weight of NaOH at 399 to 463 C (750 to 865 F) for 7-1/2 hours and then water washing gave a 90 percent yield of a product containing only 0.08 weight percent sulfur and 0.02 weight percent NaOH. In a treatment of the coke with an equal weight of NaOH at 399 to 416 C (750 to 780 F) for 2 hours, the reaction mass remained semisolid, meaning that intimate contact of the reactants was not achieved, and the product contained 1.26 weight percent sulfur.

3.3.4 Other Base Treatments

Lukasiewicz(257) has studied the use of sodium carbonate (Na_2CO_3) for the desulfurization of petroleum coke. High sulfur cokes were pulverized, mixed with Na_2CO_3, heated to the reaction temperature and maintained for some time, cooled, washed with water, and dried. The optimum reaction temperature was found to be about 760 C (1400 F), as is shown in Figure 44 for a coke made from Santa Maria Valley crude oil. The sulfur removal at that temperature was about 49 percent and the yield was about 91 percent. A 1-hour reaction time gave better desulfurization. Treating for 1 hour at 760 C (1400 F) was about as effective as treating for 4 hours at 650 C (1200 F). Other reagents from the sodium carbonate family were found to be suitable, these included sodium sesquicarbonate (trona), sodium bicarbonate, and the monohydrate and decahydrate of sodium carbonate. Potassium carbonate (K_2CO_3) was also effective. A typical material balance for the sodium carbonate treatment is given in Table 66.

Lukasiewicz also studied the addition of Na_2CO_3 to the residuum before the coking operation as a means of reducing the sulfur content of the coke. The data are shown in Table 67. About the same reduction in the sulfur content of the coke was obtained in this manner.

Titov(258) has studied the selectivity of a number of solvents for extracting porphyrin complexes from petroleum fractions. The best solvent found was N,N-dimethylformamide. This solvent was effective even at low porphyrin concentrations. With this solvent, 75 to 80 percent of the



Conditions: Santa Maria Valley coke, 60-100 mesh, 20 weight percent Na_2CO_3, 1 hour reaction time

FIGURE 44. EFFECT OF TEMPERATURE ON DESULFURIZATION OF COKE WITH SODIUM CARBONATE(257)

TABLE 66. TYPICAL MATERIAL BALANCE FOR DESULFURIZATION OF COKE WITH SODIUM CARBONATE(257)

Average of Two Runs.

Treatment Temperature = 764 C (1407 F)

Santa Maria Valley Coke

Material	Grams
In	
Coke (5.64% S)	100.0
Na_2CO_3	20.3
Total	120.3
Out	
Leached and dried coke (2.86% S)	91.0
Solids from leaching (11.0 grams total)	
Na_2S[(a)]	5.3
Other solids	5.7
Liquid (mainly water)	2.5
Gases (15.8 grams total)	
CO	8.1
CO_2	3.8
H_2S	1.0
H_2 and hydrocarbons	2.9
Total	120.3

(a) Calculated from the sulfur content of the leach water.

TABLE 67. DATA ON SODIUM CARBONATE ADDITION TO RESIDUUM PRIOR TO COKING(257)

Santa Maria Valley Residuum (6.41 Weight Percent Sulfur)

Na_2CO_3 Addition, weight percent on residuum	Coking Temperature, C (F)	Coke Yield, weight percent on residuum	S in Product Coke, weight percent	Percent Reduction in Coke S Content
None			5.64	base
3.6	471/763 (880/1405)[a]	19.7	3.43	39
5.3	761 (1401)	10.1	3.15	44
20.6	491 (916)	22.4	5.16	9
20.0	649 (1200)	16.6	3.27	42
20.2	762 (1404)	13.9	2.63	53
20.7	809 (1488)	12.4	2.96	48

(a) Na_2CO_3 was added during the coking operation at 471 C to obtain good dispersion without substantial desulfurization (see run at 491 C). The coke-Na_2CO_3 mixture was then heated to 763 C to effect desulfurization.

porphyrin complexes was removed from a petroleum fraction with three extractions and 95 to 98 percent was removed with ten extractions.

3.3.5 Mercaptan Oxidation Processes

There are a number of processes which have been used commercially to convert mercaptans in petroleum fractions into disulfides. The incentive for doing this is that the disulfides are much less odorous and corrosive than the mercaptans. These processes are not contaminant-removal processes *per se*, since the sulfur is not removed from the oil but is merely converted to another form. These processes are included in this discussion because of the possibility that they could be used ahead of another process which might be more selective for disulfides than for mercaptans. The mercaptan oxidation processes include:

- Doctor treatment
- Lead sulfide treatment
- Hypochlorite treatment
- Copper chloride treatment.

The *doctor treatment* involves contacting the oil with an alkaline sodium plumbite solution and a little elemental sulfur. The reactions are

$$2RSH + Na_2PbO_2 \longrightarrow (RS)_2Pb + 2NaOH$$

$$(RS)_2Pb + S \longrightarrow R_2S_2 + PbS\ .$$

A flow sheet for this process is shown in Figure 45. In some versions the sulfur is added after the plumbite solution. Care must be taken to match the quantity of sulfur added reasonably closely to the amount of mercaptan in the oil. The plumbite solution is prepared by adding lead oxide to a solution of 8 to 24 percent sodium hydroxide. The solution can be regenerated from the lead sulfide by air blowing the caustic solution at 65 to 80 C (150 to 175 F).(248)

Wood(233) has studied the effectiveness of sodium plumbite solutions, with and without elemental sulfur, in removing sulfur species from oil. Solutions of various single, pure organic sulfur compounds in naphtha were treated. The descriptions of the removal efficiencies given by Wood are presented in Table 68. The mercaptan was converted to the

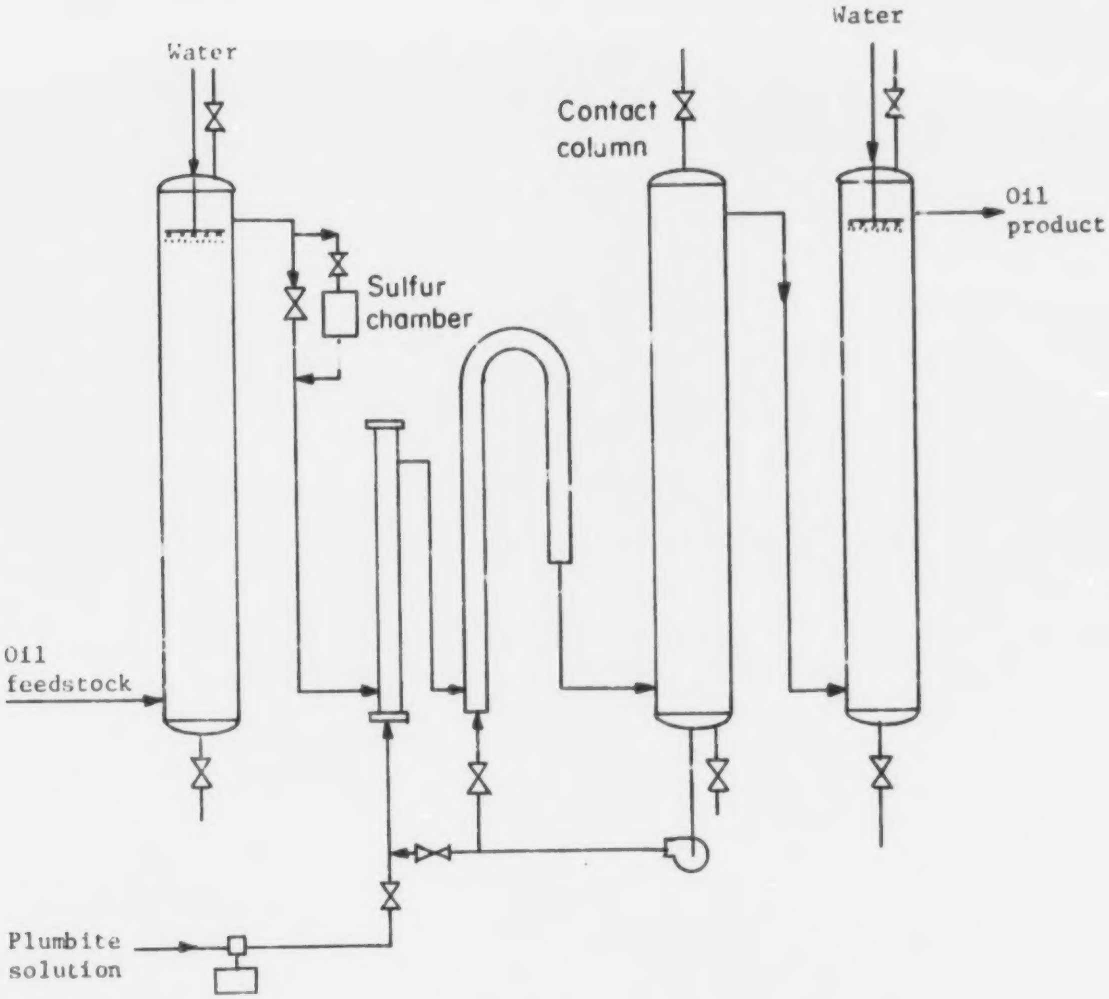

Water
Contact
column
Water
Oil
product
Sulfur
chamber
Oil
feedstock
Plumbite
solution

FIGURE 45. FLOW SHEET FOR DOCTOR TREATMENT FOR MERCAPTAN OXIDATION(248)

TABLE 68. DEGREE OF REMOVAL OF SULFUR SPECIES FROM OIL BY SODIUM PLUMBITE TREATMENT(233)

Species Contained in Naphtha Solution	Treating Agents Used	
	Na_2PbO_2	Na_2PbO_2 + S
Free sulfur	None	None
Isoamyl mercaptan	Removes partially as lead mercaptides	Forms naphtha solution of disulfides
Hydrogen sulfide	Removes as PbS	Removes as PbS
Dimethyl sulfate	Removes as $PbSO_4$	Removes as $PbSO_4$
Methyl p-toluene-sulfonate	None	None
Carbon disulfide	None	None
n-Butyl sulfide	None	None
n-Propyl disulfide	None	None
Thiophene	None	None
Diphenyl sulfoxide	None	None
n-Butyl sulfone	None	None

mercaptide and, when elemental sulfur was added, to the disulfide. The H_2S was removed as lead sulfide, and the alkyl sulfate was removed as lead sulfate.

Treatment of oil with lead sulfide can also be used to oxidize the mercaptans. The overall reaction is the same as those given for doctor treatment, but the lead sulfide may act catalytically to cause the two doctor reactions to take place simultaneously as

$$2RSH + S + 2NaOH \longrightarrow R_2S_2 + Na_2S + 2H_2O \quad .$$

The reaction may be conducted by contacting the oil, sulfur, and oxygen (air) with a solid bed of lead sulfide catalyst(259) or by recycling the lead sulfide suspended in a strong caustic solution(260) with the introduction of air and current revivification of part of the lead sulfide solution by washing with hot water.(248)

Treatment of oil with sodium or calcium hypochlorite has been used for oxidation of mercaptans in "straight-run" (uncracked) gasoline fractions, but it is seldom used for cracked products or high-boiling fractions.(248)

The "copper sweetening" process involves the oxidation of mercaptans to disulfides via the reduction of cupric chloride to the cuprous state. The reaction is

$$2RSH + 2CuCl_2 \longrightarrow R_2S_2 + 2CuCl + 2HCl \quad .$$

The regeneration step involves the oxidation of the cuprous chloride with air or oxygen:

$$2CuCl + 2HCl + 1/2\ O_2 \longrightarrow 2CuCl_2 + H_2O \quad .$$

Two versions of this process are used. The "dry process"(261) is suitable in most instances for straight-run gasoline fractions, but the "wet process" or "slurry process"(262) can be applied to a wide range of feedstocks including cracked distillates. A flow sheet for the wet process is shown in Figure 46. In this process, the oil is treated with a slurry consisting of a clay or fuller's earth, cupric chloride, and water. The feedstock is sometimes pretreated with caustic to remove H_2S and free

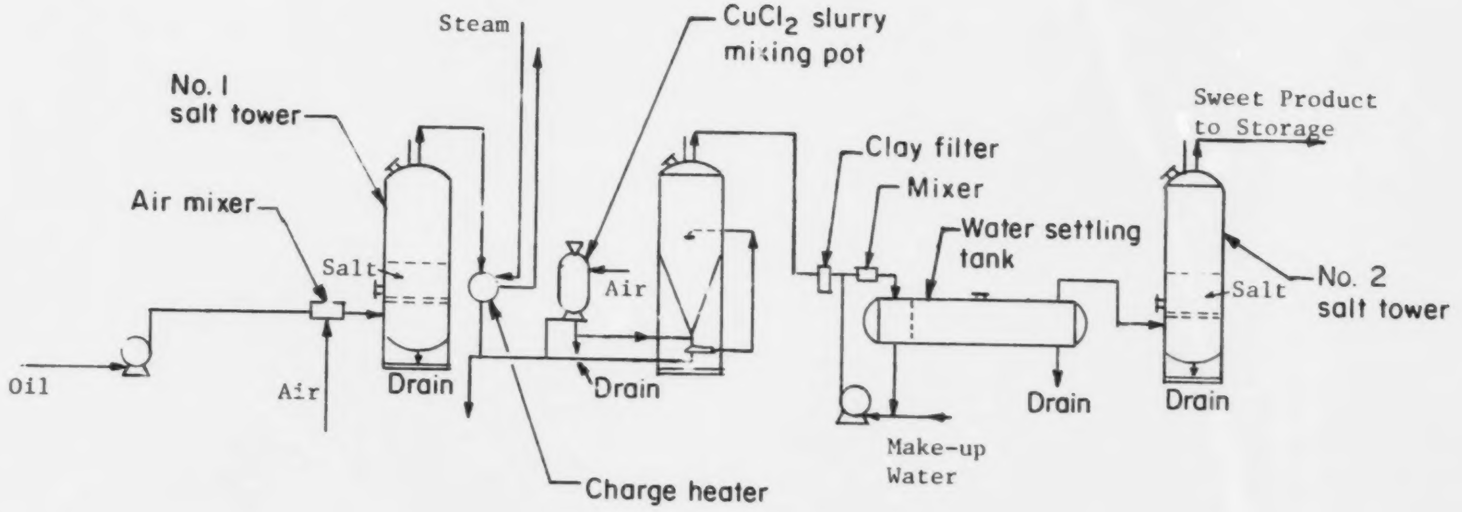

Steam
CuCl2 slurry mixing pot
No. 1 salt tower
Sweet Product to Storage
Clay filter
Mixer
Air mixer
Water settling tank
Salt
Air
Salt
No. 2 salt tower
Oil
Air
Drain
Drain
Drain
Drain
Make-up Water
Charge heater

FIGURE 46. FLOW SHEET FOR COPPER CHLORIDE WET PROCESS FOR MERCAPTAN OXIDATION(262)

sulfur, and the product oil is sometimes treated with the spent caustic wash liquid to remove traces of copper.(248)

The trend in recent years has been toward less usage of these mercaptan oxidation processes and toward more usage of hydrotreating processes, which actually remove the sulfur.

3.3.6 Selective Oxidation Plus Extraction

A patent has been issued to Guth and Diaz(263) on a process for removing sulfur and nitrogen from petroleum by a selective oxidation plus an extraction. The oxidation of the sulfur and nitrogen compounds is effected with nitrogen oxides, i.e., NO_2, N_2O_3, N_2O_4, or N_2O_5. This converts the mercaptans, disulfides, sulfides, amines, and other organic sulfur and nitrogen compounds in the feedstock into sulfoxides, aminoxides, and similar compounds which can be easily removed from the oil. Note that the oxidation products of this process are in a higher oxidation state than the disulfides produced in the processes discussed in the previous section. The inventors claim that the higher oxidation state makes the compounds easier to remove from the oil.

The extraction of the oxidized compounds is effected with a suitable solvent; methanol is the preferred one. Small quantities of methanol left in the oil product will not degrade its fuel properties. The separation of the solvent from the oil is done by gravity. Although the solvent is generally immiscible with the oil, a small amount of the oil will dissolve in the solvent. This oil can be recovered by distilling off the solvent (for recycle) and then removing the sulfur and nitrogen compounds from the concentrated oil solution by means of a hydrolysis or pyrolysis reaction.

Typical data on the sulfur and nitrogen removal possible with this process are given in Table 69. Sulfur removals up to 86 percent were obtained. The nitrogen removal is generally less than the sulfur removal, although in one run 91 percent of the nitrogen was removed. No explanation for this was given by the authors.

TABLE 69. SULFUR AND NITROGEN REMOVAL FOR NO_x OXIDATION PLUS METHANOL EXTRACTION OF OIL(263)

Feedstock	Reactor Type	Oxidation Conditions			Extraction	Percent Removal	
		Time	Temp, C (F)	Initial Volume Percent NO(a)	Volume Solvent/ Volume Oil	Sulfur	Nitrogen
Diesel oil(b)	Batch	6 hr	40 (105)	7	4	76	14
	↓	6 hr	65 (150)	5	4	66	
	↓	17 hr	65 (150)	5	4	76	
	↓	5 hr	96 (205)	5	3	76	
Diesel oil(b)	Continuous	10 min	29 (85)	5	4	43	22
	↓	12 min	77 (170)	10	3	72	91
Residual oil - 1(c)	Batch	3 hr	107 (225)	10	4	14	
	Continuous	4 min	135 (275)	10	5	86	45
Residual oil - 2(d)	Batch	7 hr	99 (210)	10	4	64	
	Continuous	8 min	65 (150)	10	5	56	
Residual oil - 3(e)	Batch	2 hr	93 (200)		4	70	

(a) The treating gas was prepared by mixing NO and air and heating the mixture to 121 C (250 F) for 30 seconds before passing the gas through the reactor.

(b) Sulfur = 0.21 weight percent, nitrogen = 0.035 weight percent.

(c) High-sulfur stock, sulfur = 2.2 weight percent, nitrogen = 2.45 weight percent.

(d) Topped Alaskan crude, sulfur = 0.36 weight percent.

(e) Kern County stock, sulfur = 1.0 weight percent.

One difficulty which can occur in this process is that some oils tend to react nonselectively during the oxidation step and form undesirable polymers and coke. This problem can be obviated by preheating the oil to 150 to 315 C (300 to 600 F) for some time, typically 2 to 20 hours, to permit the reactive groups in the oil to combine with parts of the other hydrocarbon molecules and thus to become less active. Other treatments to remove the active groups might be possible.

Very high NO_x concentrations in the oxidizer gas cannot be used because explosive mixtures could be formed with the petroleum vapors within the reactor. NO_x concentrations of 1 to 20 volume percent are recommended.

The high-sulfur, high-nitrogen oil concentrate remaining as the residue from this process can be decomposed by exposing it to air and a dilute inorganic base such as NaOH for 5 to 30 minutes at a temperature of 65 to 150 C (150 to 300 F) and a pressure of 1 to 5 atmospheres. The ensuing hydrolysis reaction decomposes the oxidized sulfur and nitrogen compounds, forming hydrocarbons, sulfite or sulfate compounds, and nitrite or nitrate compounds.

3.3.7 Sodium Treatment

The ability of metallic sodium to remove sulfur from petroleum fractions has been studied and reported since 1960.(264) A recent paper on this subject, which reviews the previous work, is that by Sternberg.(265) The two feeds used by Sternberg were:

(1) An atmospheric residuum from a California crude oil
(2) A solution of dibenzothiophene (DBT) in decahydronaphthalene.

Both feeds contained 1.65 weight percent sulfur. Some typical results are given in Table 70.

Although desulfurization with sodium is not a hydrodesulfurization, a moderate partial pressure of hydrogen must be maintained in the reaction system to prevent excessive formation of char. The hydrogen decreases the rate of desulfurization. The results indicate that treatment with sodium at 350 C (660 F) and a relatively low hydrogen partial pressure (200 psi

TABLE 70. TYPICAL RESULTS FOR TREATMENT OF OILS WITH METALLIC SODIUM(265)

Reaction Temperature = 350 C (660 F)
Sulfur in Feedstock = 1.65 weight percent

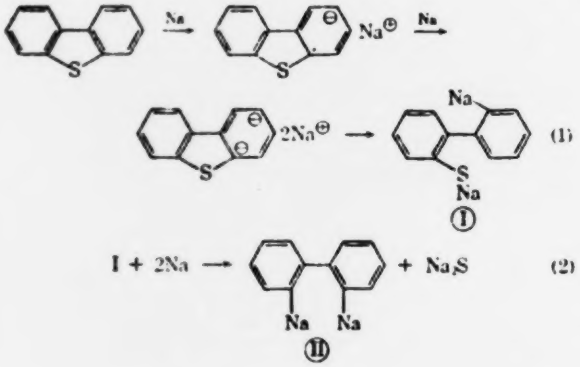
Feedstock	Na/S Ratio Weight	Na/S Ratio Molar	Gas	Gas Pressure, cold (psi)	Time, hr	Sulfur in Product, weight percent	Product Recovery,(a) percent	Sulfur Removal, percent	Char Produced, mole percent of DBT
DBT solution	2.2	3.1	N_2	100	1		91.9	>99	39.8
↓	↓	↓	H_2	200	1		90.2	99	0.7
↓	↓	↓	H_2	200	2		93.0	99	1.0
↓	↓	↓	H_2	200	6		96.2	99	14.3
↓	↓	↓	H_2	1200	1		94.8	51	Trace
↓	↓	↓	H_2	1200	2		98.7	61	Trace
↓	↓	↓	H_2	1200	6		94.0	99	0.1
Residual oil(b)	2.2	3.1	N_2	200	6	0.54	93	70	
↓	↓	↓	H_2	200	0.5	0.71	99	57	
↓	↓	↓	H_2	200	6	0.38	86	80	
↓	↓	↓	H_2	1200	0.5	1.12	100	32	
↓	3.5	4.8	H_2	200	2	0.15	100	91	
↓	4.3	6.0	H_2	200	6	0.08	74	96	

(a) For runs with dibenzothiophene (DBT) solution, this is mole percent of DBT charged. For runs with residual oil, it is weight percent of product soluble in toluene and free of material volatile below 90 C at 25 mm Hg. About half the unreacted material was char and half was material volatile below 90 C at 25 mm Hg.

(b) Atmospheric residuum from a California crude with a specific gravity of 0.990 at 15 C (60 F).

before heatup) can reduce the sulfur content of a 1.65 percent sulfur petroleum residuum to 0.3 to 0.4 percent at a Na/S mole ratio of 3.1. At higher Na/S ratios (approximately 6), the sulfur content can be reduced to less than 0.1 percent. A solution of dibenzothiophene in decahydronaphthalene can be almost quantitatively desulfurized by sodium at 350 C.

Sulfur removal by sodium treatment involves direct interaction of the sodium with the organosulfur compound. Dibenzothiophene in decahydronaphthalene solution treated with sodium metal at 350 C under nitrogen is converted to diphenyl and an insoluble char plus sodium sulfide. The reaction is highly exothermic. A possible reaction mechanism presented by Sternberg, based partially on previous work using lithium, is as follows:



The intermediate adduct II can react further either by accepting hydrogen from decahydronaphthalene or DBT to produce diphenyl and sodium or sodium hydride, or by splitting off sodium or sodium hydride and polymerizing (char formation).

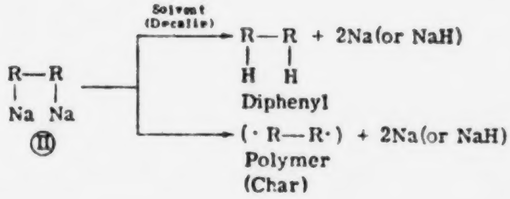
The formation of diphenyl from DBT in the absence of hydrogen gas requires an explanation. Two possible sources of hydrogen must be considered, i.e., the solvent (decalin) and its impurities (tetralin and octalin) on the one hand and DBT itself on the other. A comparison of mass spectrometric analyses of the solvent before and after the run showed that 16.8 millimoles (mmole) of H_2 was given off by the solvent. Since 36.8 mmole of diphenyl was produced in this run, the hydrogen furnished by the solvent accounts only for 46 percent of the amount of diphenyl formed. On the other hand, the conversion of DBT with an H/C ratio of

8:12 to 4.2 g char with an H/C ratio of 5:12 furnishes 42.5 mmole of H_2, more than enough to account for the 36.8 mmole of diphenyl formed. This result indicates that a substantial portion of the hydrogen required to convert the radical C_6H_4-C_6H_4 to diphenyl must have come from the conversion of DBT to char. (The 4.2 g of char produced may be viewed as consiting of a monomer with an H/C ratio of 5:12 and a molecular weight of 5H + 12C = 149. Hence, 4.2 g of char correspond to 4200/149, i.e., 28.2 mmole of $C_{12}H_5$. Since the 28.2 mmole of $C_{12}H_5$ was produced from 28.2 mmole of DBT whose H/C ratio is 8:12, it follows that this conversion liberated 3 x 28.2 x 0.5, i.e., 42.5 mmole of H_2.)(265)

In the presence of hydrogen, sodium hydride, which is formed rapidly from sodium and hydrogen at 300 C,(266,267) might replace sodium as an attacking reagent. If sodium hydride does not react as an attacking reagent, or if it reacts more slowly than sodium, then hydrogen would be expected to have an inhibitory effect on the removal of sulfur. The data in Table 70 show that hydrogen does indeed decrease the rate of desulfurization for both the DBT solution and the residual oil.

The data in Table 70 also show that the rate of sulfur removal from residual oil is much slower than that from DBT. Under identical conditions (Na/S ratio, temperature, pressure, and initial sulfur concentration), the sulfur content of the residual oil decreased by 77 to 80 percent in 6 hours, whereas that of the DBT solution decreased by 99 percent in 1 hour. Increasing the reaction time from 6 to 18 hours did not lead to any further decrease in sulfur content, whereas increasing the Na/S ratio did. These results show that lowering the sulfur content of residual oil below the 0.3 to 0.4 percent level requires an amount of sodium far in excess of that required for lowering the sulfur content from 1.65 percent to the 0.3 to 0.4 percent level. Apparently, when the reaction has reached a point where most of the reactive sulfur compounds have been desulfurized, other constituents of the residual oil, e.g., weakly acidic hydrocarbons, compete with less reactive sulfur compounds for the remaining sodium.

In this connection, it is of interest that, unlike the case of DBT in decahydronaphthalene solution, desulfurization of residual oil at longer reaction times is more effective in the presence of hydrogen than in its absence. This may be due to the fact that residual oil, having less available hydrogen than decahydronaphthalene, cannot provide the hydrogen required for hydrogenolysis of adduct II (Eq. 3) as readily as decalin.



(3)

The reduced rate of hydrogenolysis of adduct II in the absence of hydrogen may play an important role at longer reaction times, i.e., at the point where reactive sulfur-free constituents of the residual oil are beginning to compete with the less reactive sulfur containing compounds for the remaining sodium metal.(265)

3.3.8 Lithium Treatment

Treatment with metallic lithium has been studied for both desulfurization and demetallization of organic materials. The desulfurization of dibenzothiophene (DBT) with lithium has been studied by Eisch(268) and Gilman.(269,270) Eisch reacted DBT with the 2:1 lithium-biphenyl adduct at 0 C (32 F) using tetrahydrofuran as a diluent. The reaction time was 2 hours, including 1 hour to complete the addition of reactants. An 84 percent yield of 3,4-benzothiocoumarin was obtained.(268)

Gilman found that "The only product that could be isolated when dibenzothiphene was treated with lithium in dioxane and the reaction mixture was hydrolyzed was a small amount of biphenyl. When the reaction was terminated by carbonation, however, biphenyl and o-mercaptobiphenyl were obtained in about equal amounts. A two-step cleavage reaction was thus indicated."(269) The maximum yield of cleavage products was realized at a temperature of 25 C (77 F). No cleavage was obtained when ether was used in place of the dioxane, thus demonstrating "the destructive nature of refluxing dioxane on organometallic compounds".(270)

The demetallization of porphyrins by treatment with lithium has been studied by Eisner.(271) The porphyrins studied were metal derivatives of etioporphyrin I (Etio-I) and meso-tetraphenylporphin (TPP). Two methods of introducing the lithium were studied--suspensions of lithium metal in ethylenediamine and true solutions of lithium in ethylenediamine. The amount of lithium required for complete demetallization of the porphyrins was far in excess of the stoichiometric requirement. This is shown in Table 71. When smaller amounts of lithium were used the reactions did not go to completion even after prolonged boiling. The reactions did not appear to be time-dependent but either proceeded rapidly or not at all. The amount of lithium required for the various metalloporphyrins was in the order

$$VO > Ni > Co > Cu > Fe^{III}, Sn^{IV}.$$

This order agrees with the stability order for metalloporphyrins determined by other means.

3.3.9 Biochemical Treatment

An exploratory study of the use of biochemical treatment to remove sulfur from petroleum was conducted by Davis.(272) Three pure organic sulfur compounds were studied - tertiary butyl sulfide, tertiary butyl disulfide, and tertiary butyl polysulfide. The polysulfide contained and average of 4 to 5 atoms per molecule. The microorganism used was Thiobacillus thiooxidans. Growth of the bacteria was established by measurements of both sulfate (the product) and pH (sulfuric acid is a by-product).

The results indicated that the bacteria were able to attack and grow on the disulfide and polysulfide but not on the monosulfide. This implies that the bacteria were able to attack sulfur-sulfur bonds much more readily than carbon-sulfur bonds. The polysulfide was attacked more readily than the disulfide.

Two facts must be kept in mind when evaluating the feasibility of a biochemical desulfurization procedure for petroleum. First, the phenomenon observed in this study was not a removal of sulfur from oil but merely an oxidation of sulfides into sulfates. Davis stated that

TABLE 71. AMOUNT OF LITHIUM REQUIRED FOR DEMETALLIZATION OF PORPHYRINS(271)

Porphyrin Metal Species	Equivalents of Li for Complete Demetallization[a]			
	Li Metal in Ethylenediamine		Solution of Li in Ethylenediamine	
	Etio-I	TPP	Etio-I	TPP
VO^{II}[b]	2750			
Ni^{II}	2000	750	2000	1000
Co^{II}	1500	700	1500	1000
Co^{III}	1500		1500	
Cu^{II}	1000	250	1000	500
Fe^{III}	750			
Sn^{IV}	750			

(a) One equivalent of lithium means two atoms lithium per porphyrin molecule.

(b) VO^{II} is the vanadyl ion actually found in vanadium porphyrin.

"an examination of sulfate-reducing bacteria for the complete removal of sulfur is being undertaken". Second, many bacteria will decompose the oil itself (i.e., the hydrocarbons), and hence the extent of yield loss must be taken into consideration.

3.3.10 Catalytic Desulfurization

There are some processes by which light petroleum fractions (gasoline boiling range) can be catalytically desulfurized without addition of hydrogen. The sulfur compounds are converted into H_2S. This can be done only for fractions which are relatively rich in hydrogen. The processes achieve good removal of mercaptans but only partial removal of other sulfur compounds. Two processes of this type are the Perco Catalytic Process and the Gray Desulfurization Process. The Perco process uses a fixed bed of bauxite catalyst and a reaction temperature of 370 to 400 C (700 to 750 F). The catalyst can be regenerated by air burning but this is often not done because the process is used almost totally on straight run naphthas which produce little coke (10,000 to 15,000 bbl product per ton of coke). The Gray process is substantially the same except that it uses a catalyst of fuller's earth or activated clay.(273)

3.3.11 Catalytic Demetallization

Some research has been carried out on "catalytic" processes for removing metals from petroleum. The term "catalytic" is used because the intention of such a process is to remove the metals using a solid material with a composition much like a heterogeneous catalyst. The action of such a material may not be truly catalytic. An important contribution in this area is the study conducted by Hydrocarbon Research, Inc., for the EPA.(246,274,275) In the first portion of this study, 33 screening runs were conducted to test the demetallization capabilities of impregnated supports (29 runs) and supports alone (4 runs). The feedstock for these runs was a Venezuelan (Tia Juana) vacuum residuum containing 624 ppm V + Ni. The runs lasted 1 to 11 days, and both demetallization and desulfurization activities were measured. Typical run conditions included temperatures of 400 to 430 C (750 to 800 F), a pressure of 2000 psi, and liquid space velocities of 0.4 to 1 V/hr/V.

On the basis of the screening runs, activated bauxite impregnated with small amounts of molybdenum was the best overall demetallization catalyst system on the basis of both high activity and good activity maintenance. An added plus for this catalyst system is its moderately high desulfurization activity. The effects of molybdenum loading and catalyst particle size for this catalyst system are shown in Table 72. The activity does not depend strongly upon the molybdenum loading but does increase as the catalyst particle size is reduced. The maximum removal in these runs was 80 percent for vanadium and 40 percent for nickel.(274)

Hydrodesulfurization tests were run on some of the oil which had been demetallized with the molybdenum-bauxite catalyst. A 0.5 weight percent sulfur fuel oil (177 C +, 350 F +) was produced, and the activity maintenance of the hydrodesulfurization catalyst was acceptable for commercial use.

In the second phase of this study(246), three molybdenum-bauxite catalyst samples prepared on a laboratory scale by a commercial catalyst manufacturer were evaluated. Long-term aging tests showed that a catalyst containing 1.0 weight percent molybdenum was superior to a catalyst containing 0.5 percent molybdenum with respect to demetallization activity and showed slightly better aging characteristics. A 10,000-pound batch of the catalyst containing 1.0 percent molybdenum was produced by the catalyst manufacturer using commercial production equipment. This catalyst proved to be equal in all respects to the best laboratory-prepared catalyst sample. Three vacuum residua were dematallized over the commercially produced catalyst, and the demetallized products from two of the feeds were desulfurized over commercial hydrodesulfurization catalysts. The results confirmed the low catalyst deactivation rates obtained in the first phase of the program.

TABLE 72. SUMMARY OF DEMETALLIZATION SCREENING RUNS WITH MOLYBDENUM/BAUXITE CATALYST(274)

Tia Juana Vacuum Residuum

Weight Percent Mo on Catalyst	0.0		0.5		1.0		2.0	
	Percent Metals Removal at Standard Conditions							
	V	Ni	V	Ni	V	Ni	V	Ni
12 x 20 mesh support	50	20	65	35	65-70	30-40	60-65	35
20 x 50 mesh support	55	15	75	35			75-80	40

A demetallization "catalyst" of undisclosed composition (possibly similar to the above catalyst) has been used by Hydrocarbon Research, Inc., as a relatively new option for their H-Oil conversion process. Under this option, a demetallization reactor containing a "low cost solid adsorbent" precedes the conventional H-Oil reactors. The demetallizing solid, in the form of granules or powder, is continuously added to and discarded from an ebullated bed reactor.(276)

Chang(277) has studied the use of naturally occurring manganese nodules as demetallization catalysts for petroleum. Samples of manganese nodules were obtained from the Atlantic Ocean, the Pacific Ocean, and Lake Michigan. The nodule material was crushed, washed with hot water, and sieved to the 14 to 30 mesh range. The properties of the resulting catalysts are given in Table 73.

The test oil was a topped Middle East crude oil (Agha Jari) with an initial boiling point of 204 C (400 F), a specific gravity (at 60 F) of 0.91, a sulfur content of 2.2 weight percent, and metals content of 45.8 ppm V and 13.3 ppm Ni. The reaction conditions included a temperature of 399 C (750 F), a pressure of 2000 psig, a liquid hourly space velocity of 1.25, and a hydrogen circulation rate of about 10,000 scf/bbl.

The results are shown in Figure 47 as plots of demetallization and desulfurization as functions of time. As shown, high levels of demetallization activity are observed with all three catalyst samples. The nodule catalysts are only moderately active for desulfurization and essentially inactive for denitrogenation under the test conditions used. The removal of metals from the organometallic complexes presumably occurs via reduction and deposition of the metals with concurrent hydrogenation of the organic moiety. The desulfurization of petroleum is a well-known hydrogenative process. In view of this, it is interesting to note that the two ocean-nodule catalysts which contain substantial amounts of nickel, cobalt, and molybdenum (i.e., metals normally associated with hydrogenation and hydrodesulfurization activity) are less active than the freshwater nodules which contain only very low levels of these metals.(277)

TABLE 73. PROPERTIES OF CATALYSTS PREPARED FROM MANGANESE NODULES(277)

	Nodule Source		
	Pacific Ocean	Atlantic Ocean	Lake Michigan
Surface Area, m^2/g	230	226	233
Particle Density, g/cm^3	1.52	1.43	1.49
Average Pore Diameter, A	69	73	81
Pore Volume, cm^3/g	0.40	0.41	0.41
Real density, g/cm^2	3.80	3.53	3.75
Metals Analysis, weight percent			
Mn	28.5	18.8	9.2
Fe	13.9	12.3	35.4
Ni	1.21	0.72	<0.01
CoO	0.23	0.46	0.04
MoO_2	0.1	0.10	0.08

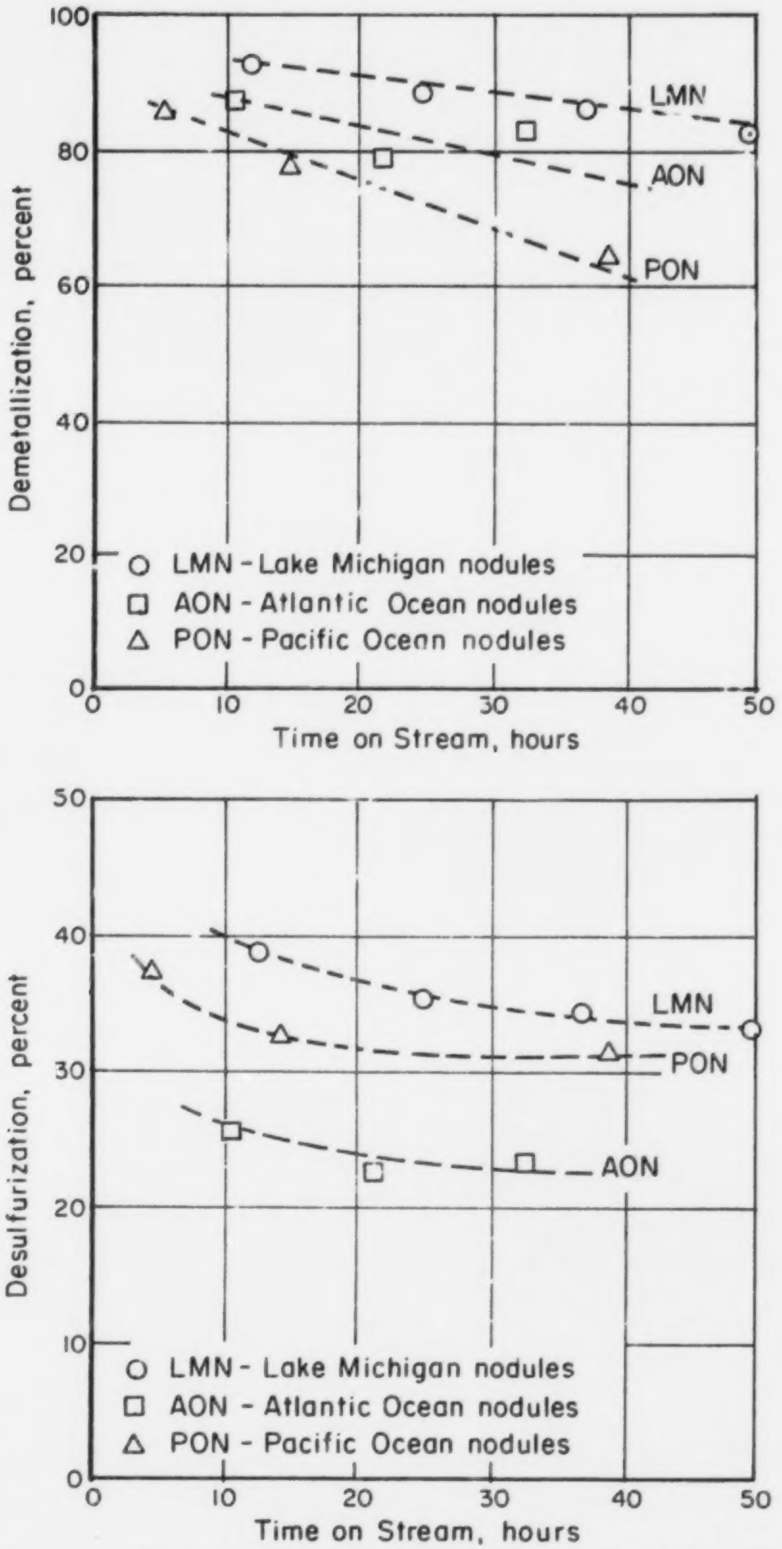


FIGURE 47. DEMETALLIZATION AND DESULFURIZATION OF OIL WITH MANGANESE NODULES(277)

Kinetic studies using two different particle sizes indicated that the demetallization reaction is adequately described by first-order kinetics and that the reaction rate is influenced by intraparticle diffusion.

A patent was issued on this method of demetallizing oil.(278)

3.3.12 Oxidative Demetallization

The use of chemical oxidants to remove metals from oil has been studied by Sugihara.(279,280) The oxidants tested included chlorine (Cl_2), sulfuryl chloride (SO_2Cl_2), dinitrogen tetroxide (N_2O_4), tert-butyl hydroperoxide, and benzoyl peroxide. The oil feedstocks were a Venezuelan (Boscan) crude oil and three asphaltene fractions separated from that crude oil by gel permeation chromatography. The results are shown in Table 74.

The data indicate that the treatments with chlorine and SO_2Cl_2 removed at least 90 percent of the prophyrins and the vanadium associated with them. The nonporphyrin vanadium does not appear to be seriously attacked under these conditions. Note that the Asphaltene Fraction III shows high vanadium removal because all of the metals content (V and Ni) of this fraction is accountable as porphyrins. The order of reactivity of the oxidants was found to be

Chlorine ≈ SO_2Cl_2 > t-butyl hypochlorite > N_2O_4
> t-butyl hydroperoxide ≈ benzoyl peroxide
≈ azobisisobutyronitrile > bromine.

Surprisingly, fluorine was found to be less reactive than chlorine.

Some experiments were also run with some synthetic, pure porphyrin compounds and their oxovanadium complexes. At given conditions, the order of reactivity was found to be

Vanadyl complex of porphyrin > free porphyrin
> diprotonated porphyrin.

Interestingly, all the synthetic vanadyl porphyrins were found to be less reactive than the petroporphyrins in the crude oil. Light accelerated

TABLE 74. VANADIUM AND PORPHYRIN REMOVAL FROM OIL BY OXIDANT TREATING(279,280)

Feedstock[a]	Oxidant	Diluent	Reaction Conditions Temp, C (F)	Reaction Conditions Time	Approximate Percent Removal of Vanadium	Approximate Percent Removal of Porphyrins
Crude oil	t-butyl hydroperoxide	None	110 (230)	22 hr	--	55
Crude oil	Cl_2	CH_2Cl_2	-78 (-108)	1 min	--	>90
Crude oil	SO_2Cl_2	CH_2Cl_2	-78 (-108)	1 min	37	90
Crude oil	SO_2Cl_2	CH_2Cl_2	-78 (-108)	5 min	60	100
Asphaltenes	Cl_2	Toluene	-78 (-108)	1 hr	50	100
Asphaltene Fract. I	Cl_2	Toluene	-78 (-108)	1 hr	48	100
Asphaltene Fract. III	Cl_2	CH_2Cl_2	-78 (-108)	1 min	93	100

(a) Feedstock concentrations in g-moles per 10^6 grams:

Feedstock	V	Porphyrins
Crude oil	22.3	10.4
Asphaltenes	70.0	29.1
Asphaltene Fract. I	75.0	15.0
Asphaltene Fract. III	72.0	79.0

all the reactions studied, but the order of reactivity given above was maintained both in the dark and in the light.(280)

In these systems, it appears that a vanadyl porphyrin or vanadyl porphyrin photochemically excited species interacts with the various reagents to form a porphyrin cation-radical, a radical, and an anion. The radical formed should attack the porphyrin cation-radical at a meso-position, which explains the relative unreactivity of tetraphenylporphines under these conditions. By shift of electrons, the positive charge of the resulting cation could be accommodated by the vanadyl group, which would have vanadium in the +5 oxidation state and a much lessened tendency to coordinate with a porphyrin. This rationalizes the extensive demetallization observed.(279)

In these experiments, the reaction mixture was quenched and washed with aqueous solutions* and water before the organic material was analyzed for its vanadium and porphyrin content. The washing removed the decomposition products from the oxidation reaction. Thus, a metals removal process based on this technology would involve two steps - the oxidation to decompose the metal-containing compounds, and a washing to remove the freed metals.

3.3.13 Treatment with Asphaltenes

Yen(281) states that for petroleum "the metals can be removed by a slurry process using asphaltenes". Although no references have been found to support the concept of removing metals from petroleum by contacting it with asphaltenes, the ability of asphaltenes to take up metals from aqueous solutions has been shown. Erdman(282) found that the asphaltene fractions of four crude oils would take up vanadium from aqueous solutions of vanadyl acetylacetonate. The amount of vanadium taken up was 800 to 2200 ppm on oil, and did not bear any significant relation to the amount of the metal originally present. The data are shown in Table 75. Limited data on nickel and copper under similar conditions indicated much less uptake of these metals from their acetylacetonate solutions.

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* A solution of 5 percent NaOH in water is given as an example but may not have been used in all runs.

TABLE 75. DATA ON UPTAKE OF METALS FROM AQUEOUS SOLUTIONS BY PETROLEUM ASPHALTENES(282)

Crude Oil Type	Boscan	LaLuma	Baxterville	Belridge
Properties of Crude Oil				
Specific gravity at 15 C (60 F)	0.952	0.885	0.959	0.974
V, ppm	1134	208	46.7	32.0
Ni, ppm	108	17.5	19.0	120.0
Asphaltenes, weight percent	18.0	4.1	17.2	5.1
Conradson carbon, weight percent	14.0	5.6	13.8	7.0
Properties of Asphaltene Fraction				
V, ppm	4480	2940	230	275
Ni, ppm			120	
Cu, ppm			12	
Percent of V present in porphyrins	19	7	~100	65
Vanadium Uptake from VO(AcAc)$_2$ Solution, ppm in oil(a)				
0.5 hr, room temp, pH = 6			2150	
0.5 hr, room temp, pH = 2	1600	1580	1170	1495
0.5 hr, room temp, pH = 0	980		810	
1-2 wks, 119 C, pH = 6			1730	
1-2 wks, 119 C, pH = 2	920		1530	
Nickel Uptake from Ni(AcAc)$_2$ Solution, ppm in oil				
8 hr, 80 C			70	
Copper Uptake from Cu(AcAc)$_2$ Solution, ppm in oil				
0.5 hr, room temp			5	

(a) Solution pH was adjusted with HCl.

The fact that petroleum asphaltenes are "unsaturated" with respect to metals and can pick up additional metals is a significant finding. However, the concept of using this phenomenon as the basis of a process for demetallizing oil evidently has not been developed. The problem is one of limiting the dissolution of the asphaltenes used for the treating into the oil being treated. It is not known whether additional work on this possibility is in progress.

3.4 Conversion Processes

There are some conversion processes used in petroleum refining which have the objective of converting heavier fuels into lighter fuels but which also effect some overall removal of contaminants from the feedstock. The degree of contaminant removal achieved in these processes is generally low. Because contaminant removal is only a secondary objective of such processes and is accomplished only to a limited extent, these processes will be considered only briefly here. The conversion processes fall into two categories - noncatalytic and catalytic.

3.4.1 Noncatalytic Processes

The noncatalytic conversion processes, or pyrolysis processes, involve the thermal decomposition of hydrocarbons into lower molecular weight hydrocarbons, which is accompanied by some polymerization of cracked products into higher molecular weight materials, i.e., tar and coke. These reactions involve primarily free-radical mechanisms, unlike most catalytic conversions which proceed via carbonium ion mechanisms. The ease of thermal cracking of hydrocarbons is in the order

olefins > paraffins > naphthenes > aromatics.

Several of the noncatalytic conversion processes do not warrant further discussion in this section. Thermal reforming of naphtha has been almost completely replaced by catalytic reforming. These naphtha reforming processes involve very little contaminant removal anyway.

Thermal cracking of gas oil has been almost completely replaced by catalytic cracking, which is discussed in the next section. Visbreaking of residuum is a mild thermal treatment used primarily to reduce the viscosity of the high-boiling components which go into fuel oil. The conditions in visbreaking are too mild to accomplish any significant contaminant removal.

Coking of residuum is a process which warrants some discussion here. In this process, residuum is converted into coke and liquid products lighter than the feed, i.e., naphtha and gas oil. Two types of processes are used--delayed coking and fluid coking. In delayed coking, the heated oil goes to an insulated soaking drum where it is held for about 1 day at about 415 to 450 C (780 to 840 F) while the drum fills up with coke. In fluid coking, the oil is fed to a fluidized-bed reactor where it is coked in a thin liquid film on small, circulating coke particles. A typical operating temperature for a fluid coker is 510 C (950 F).(283)

Some typical data on the coking of a vacuum residuum from a California crude oil are shown in Table 76.(284) For this feedstock, 21 to 41 percent of the sulfur in the feed remained in the liquid products, depending on the type of coking process used. The sulfur content of the coke was not given with these data. However, Nelson(285) gives the ratio of the sulfur content of the coke to the sulfur content of the feed for a number of feedstocks. The average value of this ratio is 1.28. Using this value, one can estimate that for the cases in Table 76, about 73 to 74 percent of the sulfur in the feed remained in the liquid products plus coke. Thus, if the rest of the sulfur is removed with the gaseous products (primarily as H_2S) the overall sulfur removal in the coking operation is no greater than about 27 percent. This general level is probably typical for most feedstocks.

3.4.2 Catalytic Processes

The catalytic conversion processes of interest from a contaminant-removal standpoint are hydrocracking, catalytic cracking, and heavy oil cracking, which is really an extension of catalytic cracking. Hydrocracking

TABLE 76. DATA ON COKING OF VACUUM RESIDUUM FROM A CALIFORNIA CRUDE OIL(284)

Feedstock Properties	
Specific gravity at 15 C (60 F)	1.032
Sulfur, weight percent	1.7
Conradson carbon, weight percent	22.5

	Delayed Coking		Fluid Coking	
	Weight Percent	Volume Percent	Weight Percent	Volume Percent
Yields				
C_3 and lighter	9.2		8	
C_4		3.4		2.2
Debutanized naphtha	20.3	28.2	14.2	19.3
Gas oil				
204-399 C (400-750 F)	26.9	31.5		--
221-546 C (430-1015 F)		--	51.1	55.0
Coke	40.2		26	
Naphtha Properties				
Specific gravity at 15 C (60 F)	0.742		0.759	
Sulfur, weight percent	0.6		0.6	
Gas Oil Properties				
Specific gravity at 15 C (60 F)	0.880		0.959	
Sulfur, weight percent	0.9		1.2	
Percent of Feed Sulfur in				
Naphtha	7.2		5.0	
Gas oil	14.2		36.1	

has been mentioned previously (under "hydrotreating") because in that process the contaminant removal is done by a normal hydrodesulfurization reactor ahead of the hydrocracking reactors. Catalytic cracking and its extension, heavy-oil cracking, are discussed here.

In catalytic cracking, the feedstock, which is some type of gas oil, is cracked over a catalyst at a temperature of 480 to 525 C (900 to 975 F) and a pressure slightly above atmospheric (5 to 10 psig).(283) The older fixed bed and moving bed systems have been mostly superseded by fluidized-bed systems. In a fluidized-bed catalytic cracker, the catalyst is continuously circulated between the reactor, where coke is deposited on the catalyst, and the regenerator, where the coke is burned off with air. The older silica-alumina catalysts have been mostly superseded by the higher activity zeolite catalysts.

Some typical data on the sulfur distribution in the products of catalytic cracking are presented in Table 77 and Figure 48.(286-288) The figure shows the effect of the conversion level in the catalytic cracker on the sulfur distribution. Most of the sulfur in the feed ends up in the fuel gas (as H_2S) or in the heavy liquid products ("cycle oil"), with smaller amounts in the gasoline and the coke laid down on the catalyst. The sulfur in the coke will be converted to sulfur oxides in the regenerator. One can see from Table 77 that for virgin gas oil feeds at the usual conversion levels [69 to 79 percent (430 F-)], 45 to 63 percent of the feed sulfur is removed either as H_2S or in coke (ultimately SO_x). Incidentally, Wollaston(286) states that the earlier thermal cracking process converted only 10 to 20 percent of the feed sulfur into H_2S.

The Heavy Oil Cracking process developed by the M. W. Kellogg Company(286,289) is an extension of fluid catalytic cracking that utilizes residuum as a feedstock. Compared with conventional gas oil cracking, the higher asphaltene content of the feed means more coke formation and the higher metals content means higher catalyst makeup requirements.

Some data on Heavy Oil Cracking of atmospheric residua are shown in Table 78.(289) The fraction of the feed sulfur which is removed as H_2S is about 43 percent for the Texas residuum and 29 percent for

TABLE 77. SULFUR DISTRIBUTION IN PRODUCTS OF FLUID CATALYTIC CRACKING[(286-288)]

Zeolite Catalysts
Virgin Gas Oil Feeds Except as Otherwise Noted

Data Source	Feed Type	Feedstock Properties		Conversion, volume percent 430 F-	Percent of Feed Sulfur Going Into				Percent of Feed Sulfur to Fuel Gas + Coke[(a)]
		Specific Gravity	Weight Percent S		Fuel Gas	Gasoline	Other Liquid Products	Coke	
Wollaston	Mid-continent	0.879	0.58	72	47	3.9	48	1.1[(b)]	48
	W. Texas	0.931	2.59	69	41	4.2	51	3.8[(b)]	45
	Hydrotreated W. Texas	0.908	0.82	74	36	2.0	60	2.0[(b)]	
	Coker gas oil	0.887	1.42	56	35	5.2	59	0.8[(b)]	
Hemler	Unspecified gas oil		1.04	80.7	48	6.5	34	9.1	57
Huling	W. Texas	0.910	1.75	77.8	42.9	3.5	48.5	5.1	48
	Hydrotreated W. Texas	0.887	0.21	77.8	19.2	2.8	69.3	8.7	
	W. Texas + coker gas oil	0.912	1.80	76.9	45.6	3.7	45.4	5.3	
	California	0.899	1.15	78.7	60.2	9.5	27.5	2.8	63
	California	0.899	1.15	84.0	62.6	8.3	23.3	5.8	
	S. Louisiana	0.918	0.46	78.1	46.5	4.4	42.5	6.6	53
	Kuwait	0.913	2.66	76.3	47.0	2.9	42.4	7.7	55

(a) Values given only for virgin gas oil feeds at usual conversion levels (69 to 79 volume percent 430 F-).

(b) By difference.

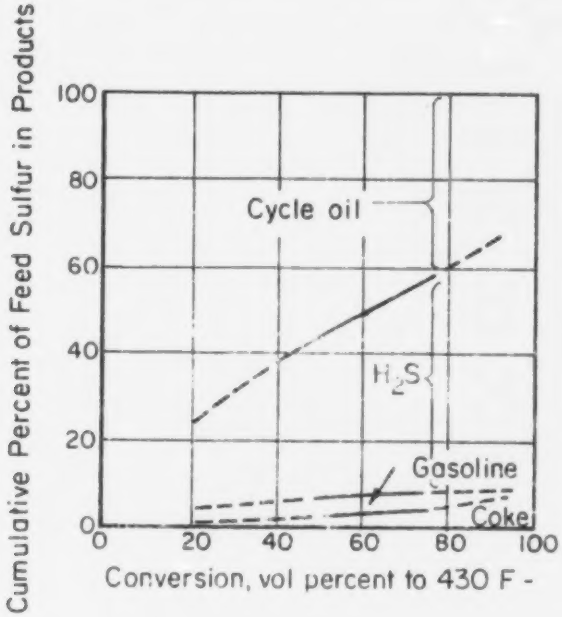


FIGURE 48. EFFECT OF CONVERSION ON SULFUR DISTRIBUTION IN FLUID CATALYTIC CRACKING OF VIRGIN GAS OILS(286)

TABLE 78. DATA ON HEAVY OIL CRACKING OF ATMOSPHERIC RESIDUA(289)

Crude Oil Source	Texas Panhandle		Gach Saran	
Feedstock Properties				
Specific gravity	0.928		0.959	
Sulfur, weight percent	1.1		2.6	
Metals, ppm	21		170	
Conradson carbon, weight percent	5.5		9.4	
Yields	Weight Percent	Volume Percent	Weight Percent	Volume Percent
C_3	4.3	7.7	3.2	5.9
C_4	6.7	10.4	3.6	5.8
Gasoline (C_5 - 400 F)	48.2	58.6	22.0	27.6
Light cycle oil	15.3	16.0	20.9	22.7
Heavy cycle oil	--	--	24.8	24.6
Decanted oil	4.7	4.0	5.9	5.6
Coke	15.7		15.5	
H_2S	0.5		0.8	
C_2 and lighter	4.6		3.3	
	100.0		100.0	
Sulfur Content, weight percent				
Gasoline	0.09		0.35	
Light cycle oil	1.0		1.3	
Heavy cycle oil	--		2.4	
Decanted oil	2.3		3.1	
Percent of Feed Sulfur in				
H_2S	43		29	
Gasoline	4		3	
Light cycle oil	14		11	
Heavy cycle oil	--		23	
Decanted oil	10		7	
Coke, by difference	29		27	
	100		100	

the higher sulfur Iranian (Gach Saran) residuum. The coke production is high (about 16 weight percent on feed) and this coke contains a large fraction of the feed sulfur (27 to 29 percent). The sulfur in the coke will be converted to sulfur oxides in the regenerator. Counting this also as removed sulfur, the overall sulfur removal by the process is about 72 percent for the Texas residuum and 56 percent for the Iranian residuum.

Although no specific data on metals removal were given for the Heavy Oil Cracking examples of Table 78, Finnegan(289) states that "the metal content of the feedstock is deposited quantitatively on the catalyst". These metals have an adverse effect on the catalyst performance by promoting coke and gas formation at the expense of liquid-products yield. The catalyst makeup requirement depends on the metals content of the feedstock. For the examples of Table 78, the catalyst requirements are 0.6 to 0.7 lb/bbl feed for the Texas residuum and 1.8 to 2.0 lb/bbl feed for the Iranian residuum.(289)

3.5 Gasification

An alternative to removing the contaminants from a liquid fuel is the possibility of gasifying the fuel and then removing the contaminants. As is true for coal, a heavy petroleum fraction such as residuum can be gasified with steam and air or oxygen to produce a fuel gas containing H_2, CO, and CH_4. During the gasification, essentially all the sulfur and nitrogen in the fuel are converted to H_2S and NH_3. Many of the metals are removed as an ash. The gas can be scrubbed or otherwise treated to remove the H_2S, NH_3, and other contaminants and then leave as a clean fuel gas.

Unlike the gasification of light petroleum fractions (methane through naphtha), the gasification of heavy fractions such as residuum is a relatively new practice. However, at least most of the steps involved are considered proven technology because of their use in other processes. Much of the research in this area is proprietary to individual oil companies. Two processes which are offered commercially are the Shell Gasification process and Texaco's Synthesis Gas Generation process.

3.5.1 Shell Gasification Process

The Shell Gasification process(290) involves a partial oxidation of the feedstock using either oxygen or air. The overall reaction can be written as:

$$C_nH_m + n/2\ O_2 \rightleftarrows n\ CO + m/2\ H_2.$$

This equation represents the net effect of a number of reactions which include:

- Complete combustion of part of the hydrocarbon to CO_2 and H_2O
- Cracking of the hydrocarbon to form methane and elemental carbon
- Reaction of CO_2 and H_2O with the hydrocarbon and with the elemental carbon to form CO and H_2.

The heat released by the exothermic combustion reaction provides the heat necessary for the other reactions, which are endothermic. The final gas composition is essentially the equilibrium composition, and this can be adjusted by changing the oxygen/fuel ratio and by adding steam to moderate the reaction temperature.

A flow sheet for the Shell Gasification process is shown in Figure 49. The four sections of the process are the gasification reactor, the waste-heat boiler, the carbon-recovery section for removing solids from the gas, and the soot recovery/recycle system for disposing of the carbon. The gasification reactor is a vertical, refractory-lined, pressurized combustion chamber with no internal baffles or catalyst beds. The gasification temperature is generally 1200 to 1500 C (2200 to 2800 F), and the residence time in the reactor is about 5 seconds. Gasification pressures up to 850 psia have been demonstrated.

For heavy feedstocks, up to 5 percent of the carbon content of the feedstock leaves the gasification reactor as solid carbon or soot. Shell has developed a helical tube design for the waste-heat boiler to avoid the potential plugging and hot-spot problems from these solids. The soot is removed from the gas by water scrubbing. Shell offers two routes for recovering the soot from the wash water - the Shell Pelletizing process and the Shell Closed Carbon Recovery process. In the pelletizing

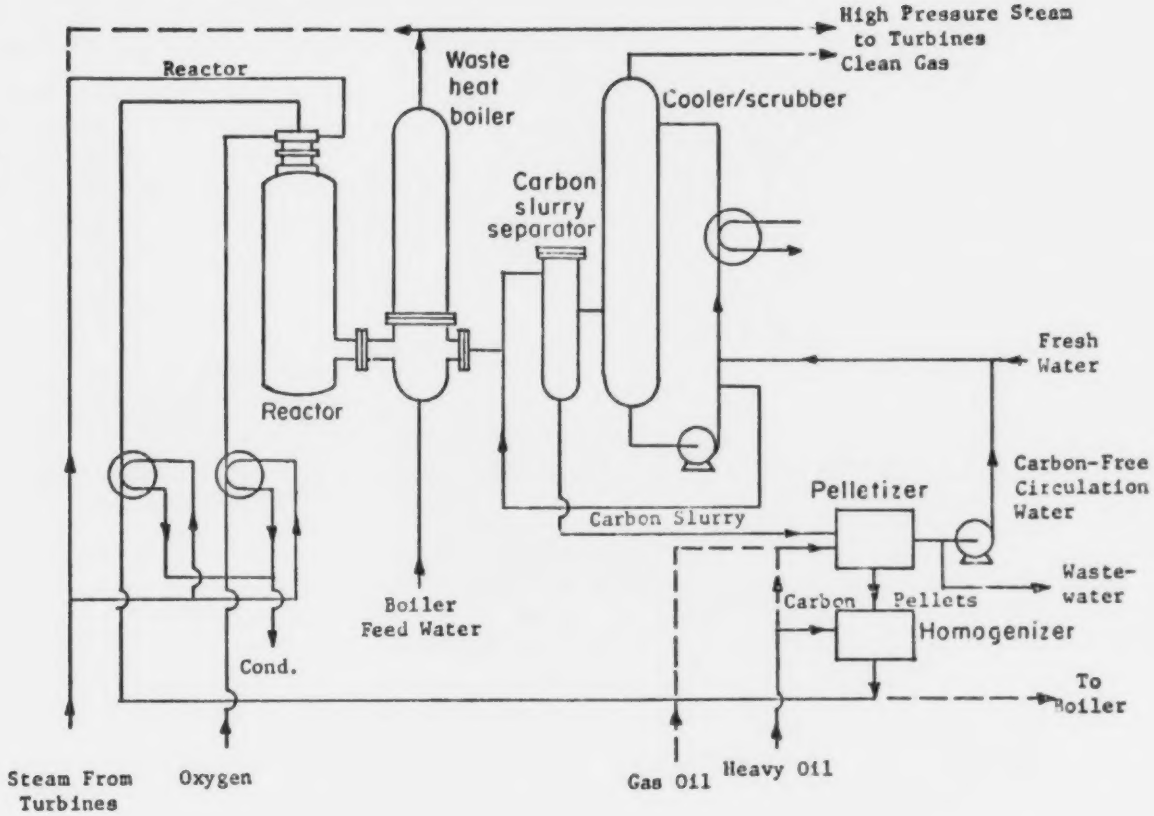

High Pressure Steam to Turbines
Clean Gas
Reactor
Waste heat boiler
Cooler/scrubber
Carbon slurry separator
Fresh Water
Reactor
Carbon-Free Circulation Water
Pelletizer
Carbon Slurry
Waste-water
Carbon
Pellets
Homogenizer
Boiler Feed Water
Cond.
To Boiler
Steam From Turbines
Oxygen
Gas Oil
Heavy Oil

FIGURE 49. FLOW SHEET FOR SHELL GASIFICATION PROCESS(290)

process, a low-viscosity oil is used to preferentially wet the soot particles so that they can be formed into pellets which can be homogenized into the oil feed to the gasifier or can be used directly as a low-sulfur fuel. In the closed carbon-recovery process, the soot is extracted from the water with naphtha, the naphtha-soot extract is mixed with the oil feed, and the mixture is fractionated to recover the naphtha for recycle, thus leaving the soot in the oil feed to the gasifier.(290)

3.5.2 Texaco Process

The Texaco Synthesis Gas Generation process(291,292) is quite similar to the Shell process. A flow sheet for the Texaco process is shown in Figure 50. In this process, 1 to 3 percent of the feedstock is converted to soot, and a naphtha extraction system is used to transfer the soot from the wash water to the oil feed for recycle to the gasifier. Gasification temperatures range from 1100 to 1600 C (2000 to 2800 F) and pressures from nearly atmospheric to over 2000 psig.

3.5.3 Chemically Active Fluid-Bed Process

Another approach to the conversion of heavy oil is the Chemically Active Fluid-Bed process being developed by Esso Petroleum Company, Ltd. (Abington, England) and includes a group with EPA funding.(293) This process involves the partial combustion of oil in a fluidized bed of lime. The H_2S formed during this combustion reacts with the lime, thus yielding a clean fuel gas in one step. The sulfided lime can be either disposed of in a once-through type of operation or regenerated in a second fluidized bed to produce an SO_2-rich stream and lime for recycle. The recovered SO_2 can be converted to elemental sulfur or sulfuric acid. A flow sheet of this process is shown in Figure 51.

The gasifier operates at a temperature of about 880 C (1620 F) and the regenerator at about 1080 C (1970 F).

The experimental work to date on this process has been carried out on a 0.75-megawatt equivalent pilot plant. Additional work is in progress on a demonstration plant, which will include the regeneration and sulfur recovery.

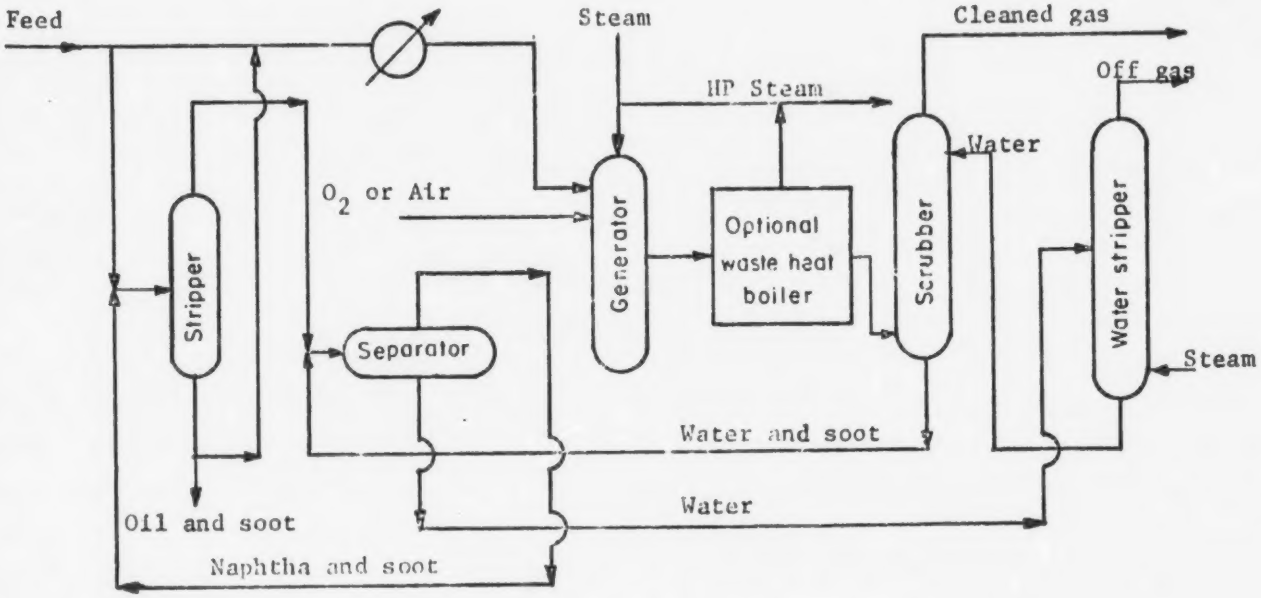

Feed
Steam
Cleaned gas
HP Steam
Off gas
Water
O$_2$ or Air
Stripper
Separator
Generator
Optional waste heat boiler
Scrubber
Water stripper
Steam
Water and soot
Oil and soot
Water
Naphtha and soot

FIGURE 50. FLOW SHEET FOR TEXACO SYNTHESIS GAS GENERATION PROCESS(292)

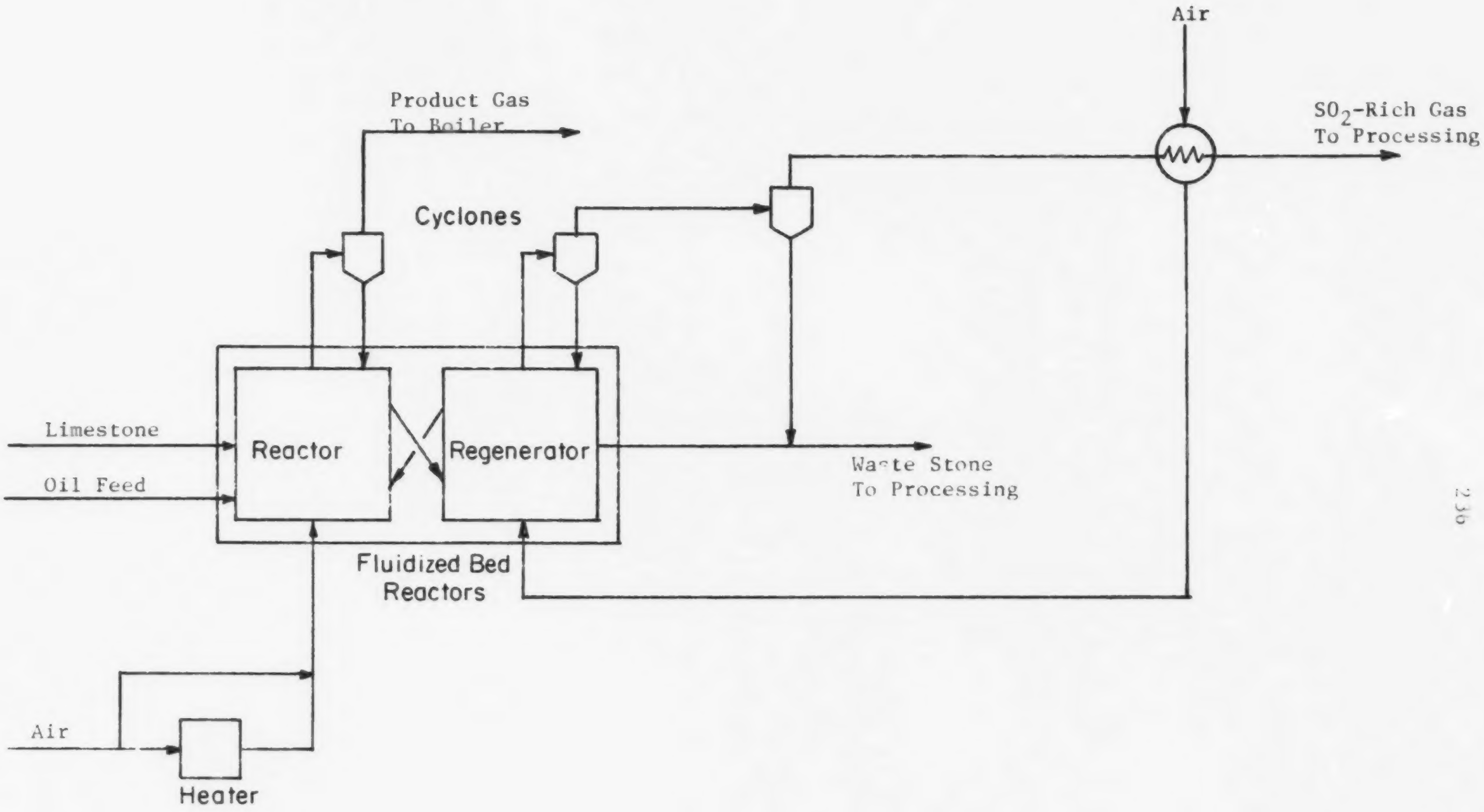

Air
Product Gas
To Boiler
SO_2-Rich Gas
To Processing
Cyclones
Limestone
Oil Feed
Reactor
Regenerator
Waste Stone
To Processing
Fluidized Bed
Reactors
Air
Heater

FIGURE 51. FLOW SHEET FOR CHEMICALLY ACTIVE FLUID BED PROCESS(293)

The pilot-plant studies have demonstrated the ability of the process to achieve 90 percent sulfur removal, essentially complete vanadium removal, 75 percent nickel removal, and 40 percent sodium removal.(293)

Since the clean fuel gas is produced at a high temperature, the process is best suited for applications in which the gas is burned at the same site, thus avoiding cooling and reheating.

3.5.4 Coking Plus Gasification

Still another approach to gasification is the Flexicoking process being developed by Exxon.(294-296) In this process, high-sulfur residuum is fed with steam into a fluidized-bed coker where it is converted into coke plus liquid and gaseous products. The coke then goes to a fluidized-bed reactor in which it is gasified with air and steam to produce a low-Btu gas. This gas is then treated to remove H_2S and NH_3. Overall, 98 to 99 weight percent of the feed is converted into gaseous and liquid products, and the metals are concentrated in a 1 to 2 weight percent solids purge. Thus, a combination of coking and coke gasification is used to achieve the conversion of a liquid fuel to a gaseous fuel. A flow sheet for this process is shown in Figure 52. Note that a third fluidized-bed vessel is required between the coker and the gasifier for heat-transfer purposes.

The Flexicoking process does yield some products other than the fuel gas, as illustrated by the data in Table 79. For the feedstock considered here, 54 percent of the feed is converted into lighter liquid products (naphtha and gas oil) which require further processing (normally hydrotreating) for sulfur removal. About 34 percent of the feedstock is converted to coke, and about 20 percent of the energy in the feedstock ends up in the gas produced by gasifying that coke.

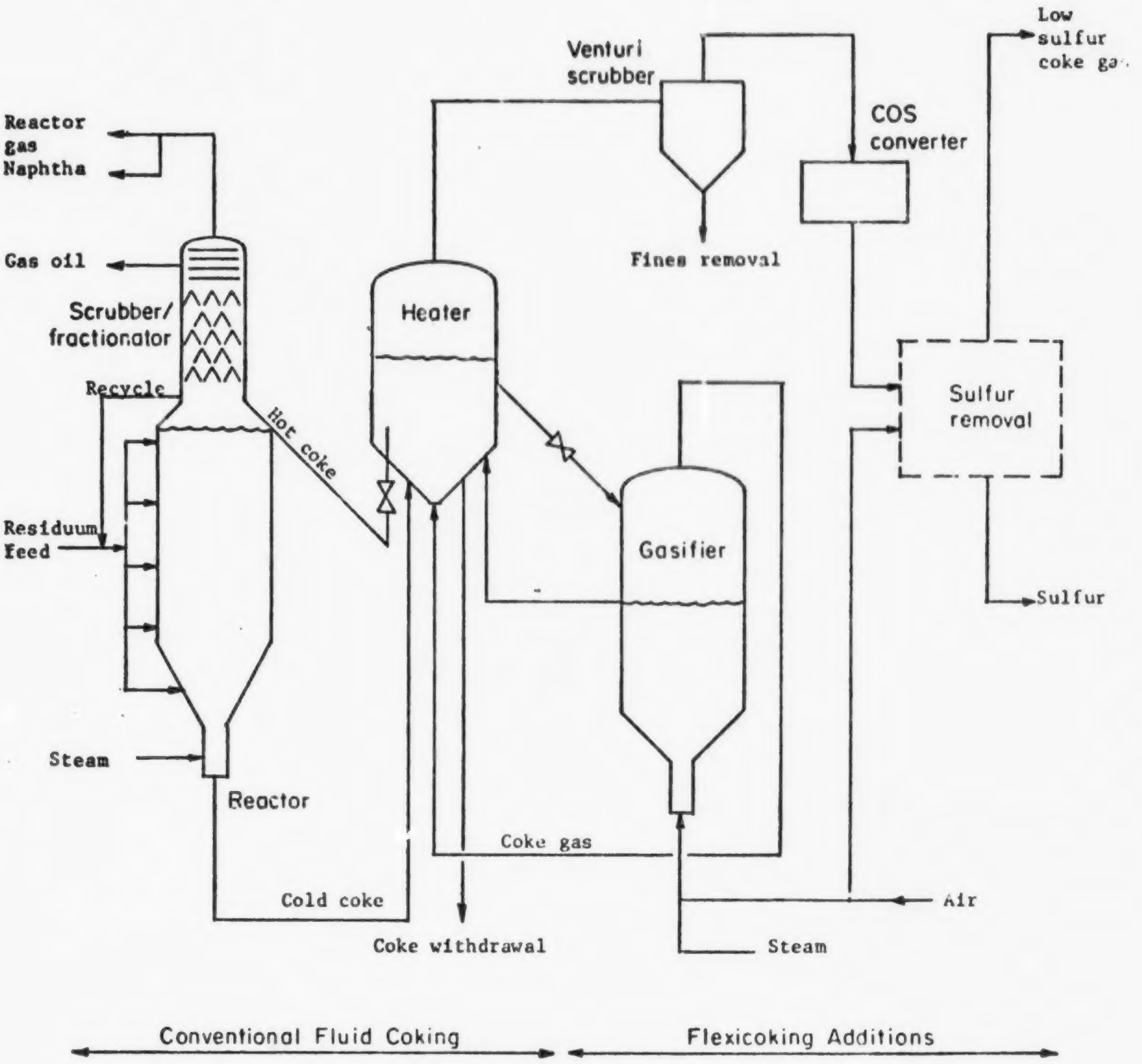
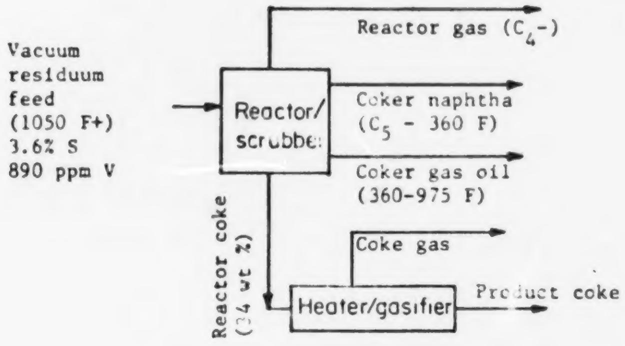

Low sulfur coke ga.
Venturi scrubber
COS converter
Reactor gas
Naphtha
Gas oil
Fines removal
Scrubber/ fractionator
Heater
Sulfur removal
Recycle
Hot coke
Residuum feed
Gasifier
Sulfur
Steam
Reactor
Coke gas
Cold coke
Air
Coke withdrawal
Steam
Conventional Fluid Coking
Flexicoking Additions

FIGURE 52. FLOW SHEET FOR FLEXICOKING PROCESS (294)

TABLE 79. TYPICAL YIELD DATA FOR FLEXICOKING OF BACHAQUERO VACUUM RESIDUUM(295)


Vacuum residuum feed (1050 F+) 3.6% S 890 ppm V
Reactor/scrubber
Reactor gas (C_4-)
Coker naphtha (C_5 - 360 F)
Coker gas oil (360-975 F)
Reactor coke (34 wt %)
Coke gas
Heater/gasifier
Product coke

Product	Yield on Feed Weight Percent	 Volume Percent	 Other	Percent of Sulfur in Feed	Sulfur Content As-Is	 After Desulf[(a)]	Product Quality
Reactor gas	13			25	7%	Nil	1300 Btu/scf
Coker naphtha	10	15		-2	0.7%	<0.07%	
Coker gas oil	44	48		36	3.1%	<0.3%	Sp Gr = 0.97
Coke gas			0.2 FOEB/ bbl feed(b)	36	<170 ppm		125 Btu/scf
Product coke	1.5			-1	<2%		-6%V

(a) Based on typical desulfurization in downstream processing facilities.

(b) FOEB = fuel oil equivalent barrel = 6.3 x 10^6 Btu.

3.5.5 Efficiency

The primary drawback to the gasification route is the relatively low efficiency of this fuel conversion. As an example, for the Shell Gasification process, 65 to 75 percent of the feedstock heating value is recovered in the fuel gas when the gasification is done with air. For gasification with oxygen, the range is 75 to 85 percent.(291) These efficiencies are comparable to those for coal gasification. Of course, any contaminant-removal process requires some energy and thus has an efficiency less than 100 percent, but one would have to say that gasification is a rather extreme method of removing impurities from a liquid or solid fuel.

3.5.6 Other Considerations

An advantage of the gasification route is that it permits essentially complete elimination of the fuel-related pollution. The fuel produced can contain essentially no sulfur, nitrogen, or ash. A limitation to this route is that without upgrading by methanation (which further decreases the efficiency) the gas cannot economically be transported over long distances. Related to these points is the fact that the economics of gasification are such that it is feasible only for relatively large-scale users or for groups of smaller users close enough to share a common gasification facility.

3.6 Summary of Removal Methods

The methods of removing contaminants from petroleum are summarized in Table 80. When known, the general degree of contaminant removal is indicated by a + (substantial removal) or a - (negligible removal). Limitations on the types of contaminants which can be removed are specified in the footnotes. The only processes which have been proven capable of effecting substantial removal of all three contaminants (sulfur, nitrogen, and metals) are hydrotreating and gasification.

TABLE 80. METHODS OF REMOVING CONTAMINANTS FROM PETROLEUM

		Contaminant Removal[a]		
	Removal Method	Sulfur	Nitrogen	Trace Elements
I.	Physical Methods			
	Water washing	-	-	+
	Filtration			+
	Centrifugation			+(b)
	Adsorption	+		
	Solvent deasphalting			+
	Stripping	+(c)	+(c)	
II.	Hydrotreating	+	+	+
III.	Chemical Refining			
	Sulfuric acid treatment	+		
	Other acid treatments		+	+
	Caustic treatment	+(d)		
	Other base treatments			+
	Mercaptan oxidation processes	-(e)		
	Selective oxidation plus extraction	+	+	
	Sodium treatment	+		
	Lithium treatment			+
	Biochemical treatment	-(f)		
	Catalytic desulfurization	+		
	Catalytic demetallization			+
	Oxidative demetallization			+
	Treatment with asphaltenes(g)			
IV.	Conversion Processes			
	Noncatalytic processes	+(h)		
	Catalytic processes	+		
V.	Gasification	+	+	+

(a) Plus (+) = all or part (normally >50 percent); negative (-) = negligible removal.

(b) Mixed results for conventional centrifugation; definite result for ultracentrifugation.

(c) Only gaseous contaminants are removed (Sulfur present as H_2S, nitrogen present as NH_3)

(d) Only H_2S, mercaptans, and some sulfates are removed.

(e) Mercaptans are oxidized to disulfides but no sulfur is removed.

(f) Sulfides are oxidized to sulfates but no sulfur is removed.

(g) Concept which might serve as basis for metals-removal process.

(h) 20 to 30 percent sulfur removal in coking process.

4.0 METHODS OF REMOVING CONTAMINANTS FROM TAR SAND OIL AND SHALE OIL

4.1 Introduction

Tar sand and oil shale are energy resources which are capable of yielding fuel products much like those produced from petroleum. Raw (untreated) tar sand oil and raw shale oil are liquid fuels similar in many respects to crude petroleum, although the contaminant levels are generally higher. Like crude petroleum, the raw tar sand oil and shale oil will generally not be used for fuels as such but will be fractionated into various boiling ranges and treated in various ways (before or after fractionation) to upgrade them into a number of salable fuel products. Many of these products will be essentially indistinguishable from those products obtained from petroleum. The treatment steps employed will include processes in which contaminants such as sulfur, nitrogen, and metals are removed from various hydrocarbon streams. It is the intention of those who are planning for the development of these resources (only one tar sand facility is in operation) that the contaminant-removal processes employed will be basically the same as those used for petroleum. There are, of course, differences between petroleum and tar sand oil and between petroleum and shale oil, and these differences may require different operating conditions and perhaps reoptimization of other process variables. Defining the optimum process variables and the possible extent of removal for new feedstocks requires experimental studies, but the situation differs only in degree from that for petroleum itself, since significant differences exist among different crude oils.

The discussion of contaminant-removal processes for petroleum in the previous section thus provides the basis for a consideration of processes for removing contaminants from tar sand oil and shale oil. The discussion in this section reviews the work which has been done in applying the removal processes to tar sand oil and shale oil. Ways in which the differences between these materials and petroleum would be expected to impact on the operation and effectiveness of the various removal methods are considered. Tar sand oil and shale oil are discussed separately below.

4.2 Tar Sand Oil

4.2.1 Differences from Petroleum

Tar sand oil has a higher C/H ratio and is more viscous than most petroleum crudes, also, the tar-sand-oil fraction which is low in paraffinic constituents contains saturated single-ring compounds (naphthenes). The heavier fractions of tar sand oil (final boiling point up to 538 C) contain condensed-ring aromatic compounds, some containing more than 40 rings. The asphaltene content of the Athabasca tar sand is about 17 percent. The sulfur and nitrogen contaminants are predominantly of a heterocyclic nature. The oil produced from some Canadian tar sands may be relatively low in sulfur content, but the oil from U.S. tar sands contains more sulfur than most petroleum crudes.

Overall, one can say that tar sand oil is more similar to petroleum crude than is shale oil. This is reflected in the fact that for both tar sand oil and petroleum the major contaminant to be removed is sulfur.

4.2.2 Commercial and Planned Commercial Processing

There is one commercial tar sand processing plant now in operation [owned by Great Canadian Oil Sands, Ltd. (GCOS)]. Several other plants are in the planning stage. For separation of the bitumen from the sand, the GCOS plant uses a hot water-plus-caustic treatment followed by skimming and froth flotation and a dilution-plus-centifuging treatment of the froth. Essentially the same process is planned for the future facilities. Separation of the sand from the oil is not considered a contaminant-removal process in the scope of this study, so this will not be discussed further.

For "upgrading" of the tar sand oil, the GCOS plant uses delayed coking plus hydrotreating of the resulting liquid products. Two of the planned facilities (Syncrude Canada, Ltd. and Petrofina Canada, Ltd.) also include coking plus hydrotreating, but in these plants, fluid coking will be used. Another planned facility (Home Oil/Alminex) includes Flexicoking plus hydrotreating. The only planned facility which does not include some type of coking as the primary step is the Shell Canada, Ltd., plant which is to use vacuum distillation, solvent deasphalting, and hydrotreating.(297,298) One reason for the attractiveness of coking as the primary step is that the tar sand oil still contains small amounts of fine sand, and this material is readily removed with the coke.

Some data are available on the two general categories of processing used or intended for use on tar sand oil - hydrotreating and coking.

4.2.3 Hydrotreating

The Canadian Department of Energy, Mines and Resources has studied the hydrotreating of tar sand oil. One should keep in mind that these data are for Canadian tar sands, although the performance on U.S. tar sands should be similar.

Takematsu(299) has studied the hydrotreating of a heavy gas oil produced by coking of Athabasca tar sand oil. A commercial cobalt-molybdate catalyst was used. A system in which the oil flowed upward through the catalyst bed cocurrent with the hydrogen was found to be superior to a downflow, countercurrent system. The data are shown in Table 81. With the upflow system, sulfur removals of over 90 percent were achieved. In the upflow system, any low-boiling material present in the feed or produced in the course of reaction vaporizes and quickly leaves the reactor, whereas the high-boiling material has a long residence time in the reactor. The following studies were also made with the downflow system.

Soutar(300) has studied the effect of the mineral matter (sand) content of the tar sand oil on the hydrotreating operation. The data are shown in Figure 53. The sulfur removal decreases as the mineral content of the feed is increased, evidently because of partial poisoning of the catalyst by minerals deposited on it. The sulfur removal increases as the operating temperature is increased. The raw

TABLE 81. DATA ON HYDROTREATING OF TAR SAND OIL(299)

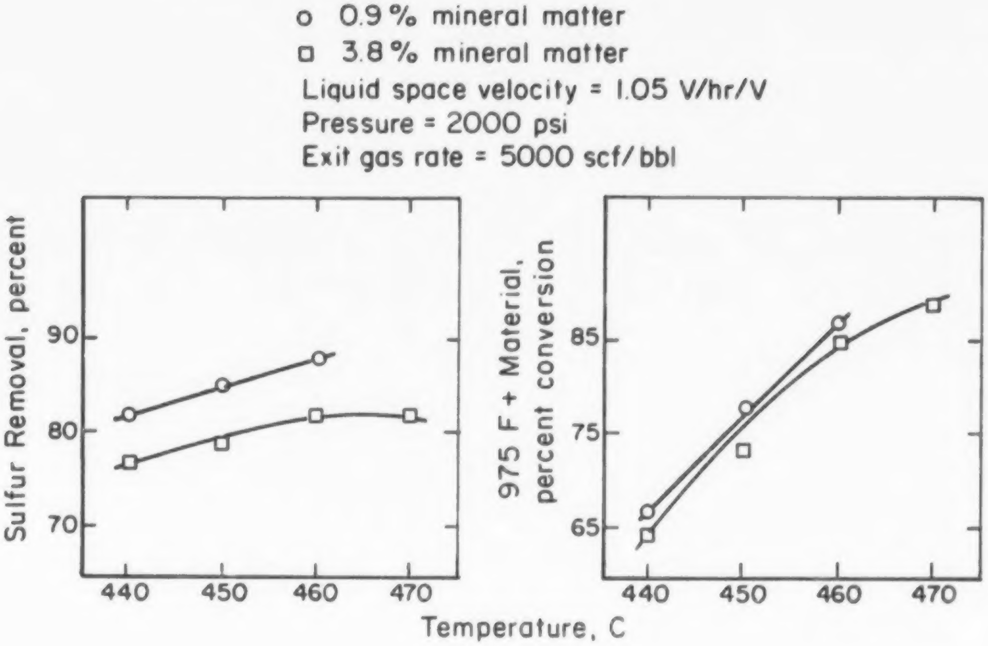
Feedstock: Heavy gas oil (90 percent 200 to 400 C) from delayed coking of Athabasca tar sand oil

3.38 weight percent sulfur, 0.26 weight percent nitrogen, 0.21 weight percent Conradson carbon, 0.004 weight percent ash, 2 ppm V, specific gravity at 60 F = 0.950

Catalyst: Commercial cobalt-molybdate

Reaction Conditions(a)					Yield on Feed	
Oil Flow Direction	Exit Gas Rate, scf/bbl	Temperature, C	S in Product, weight percent	Sulfur Removal, percent	Weight Percent	Volume Percent
Upward	4000	360	0.34	90.2	97.7	103
↓	↓	380	0.18	94.7	97.7	103
		400	0.12	96.5	97.6	104
Downward	7500	370	0.91	73.7	98.1	103
↓	↓	390	0.53	84.6	97.8	103

(a) Other reaction conditions were a pressure of 2000 psi and a liquid space velocity of 1 $ft^3/hr/ft^3$ catalyst.



Feedstock Properties	0.9% Mineral Matter Feed	3.8% Mineral Matter Feed
Sulfur, weight percent	4.72	4.77
Nitrogen, weight percent	0.38	0.52
V, ppm	189	180
Ni, ppm	68	70
Weight percent 524C+ (975 F+)	51	51

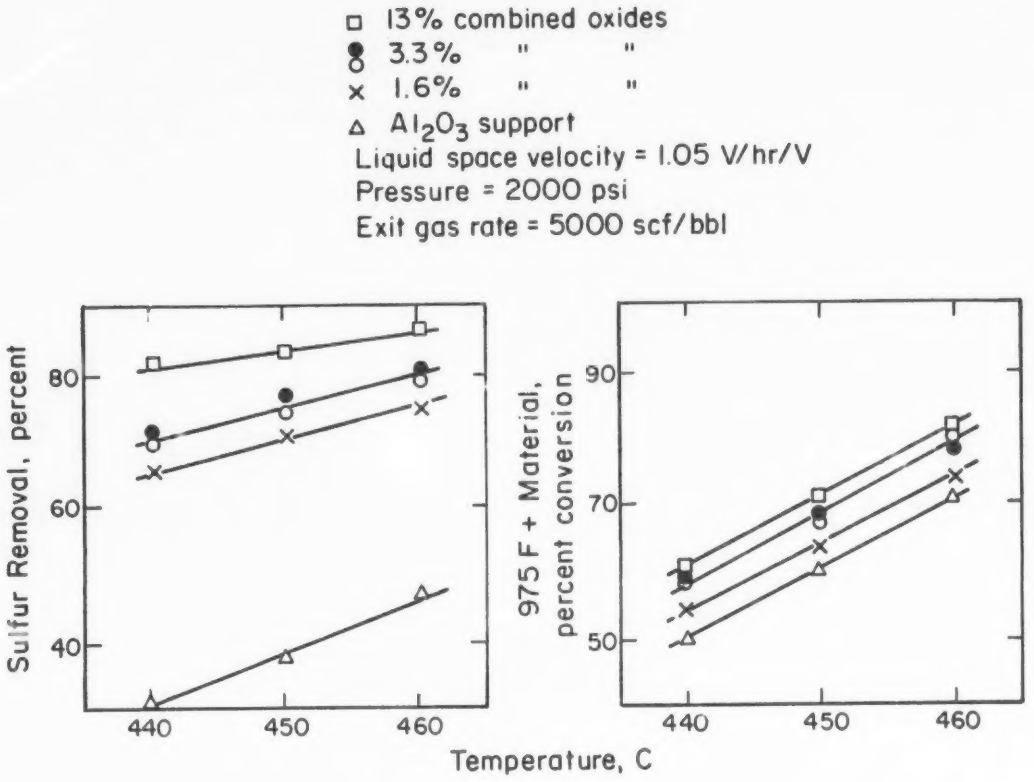
FIGURE 53. EFFECT OF MINERAL MATTER CONTENT OF TAR SAND OIL ON HYDROTREATING(300)

tar sand oil feeds used in this study are considerably harder to desulfurize than the gas oil fraction studied by Takematsu. Note that the maximum sulfur removal obtained with these feeds was about 88 percent. The severity of the operation is reflected by the conversion of heavy feed components (524 C+) to light species (524 C-), which is shown on the right-hand plot.

McColgan(301) has studied the effect of the catalyst metals loading (cobalt and molybdenum oxides) on the hydrotreating operation. The data are shown in Figure 54. In preparing these catalysts, the cobalt and molybdenum oxides were put only on the outer surfaces of the alumina support particles in order to obtain higher activity. The sulfur removal increases as the catalyst metals loading is increased. Raw tar sand oil was used as the feedstock in this study, and the maximum sulfur removal obtained was about 85 percent.

Nitrogen removal during the hydrotreating of tar sand oil has been studied by Williams.(302) The feedstock used was a heavy gas oil fraction (343 to 524 C or 650 to 975 F) from an Athabasca tar sand oil. The results are shown in Figures 55 and 56. The maximum sulfur removal obtained was about 93 percent, whereas the maximum nitrogen removal was only 68 percent. These values are typical of the performance for hydrotreating of most petroleum gas oils. The data indicate that as the catalyst metals loading was increased the denitrogenation activity increased more slowly than the desulfurization activity. Also, as shown in Figure 56, the optimum Co/Mo ratio on the catalyst may be somewhat higher for denitrogenation than for desulfurization.

In addition to the work on catalytic hydrotreating, the Canadian Department of Energy, Mines and Resources has also studied the thermal hydrotreating of tar sand oil. Some data are presented in Figure 57.(302) As expected, this process is less effective in removing contaminants than the catalytic process. The maximum sulfur removal obtained in this study was about 45 percent, compared with 88 percent for the catalytic process (Figure 56). Note that the sulfur removal is not appreciably affected by the mineral content of the oil. In this process there is no catalyst to be poisoned by the minerals. On the other hand, the minerals themselves apparently do not catalyze the sulfur removal reactions. In



Feedstock Properties: 4.72% S, 0.38% N, 189 ppm V, 68 ppm Ni, 51 weight percent 524 C+ (975 F+)

FIGURE 54. EFFECT OF CATALYST METALS LOADING ON HYDROTREATING OF TAR SAND OIL (301)

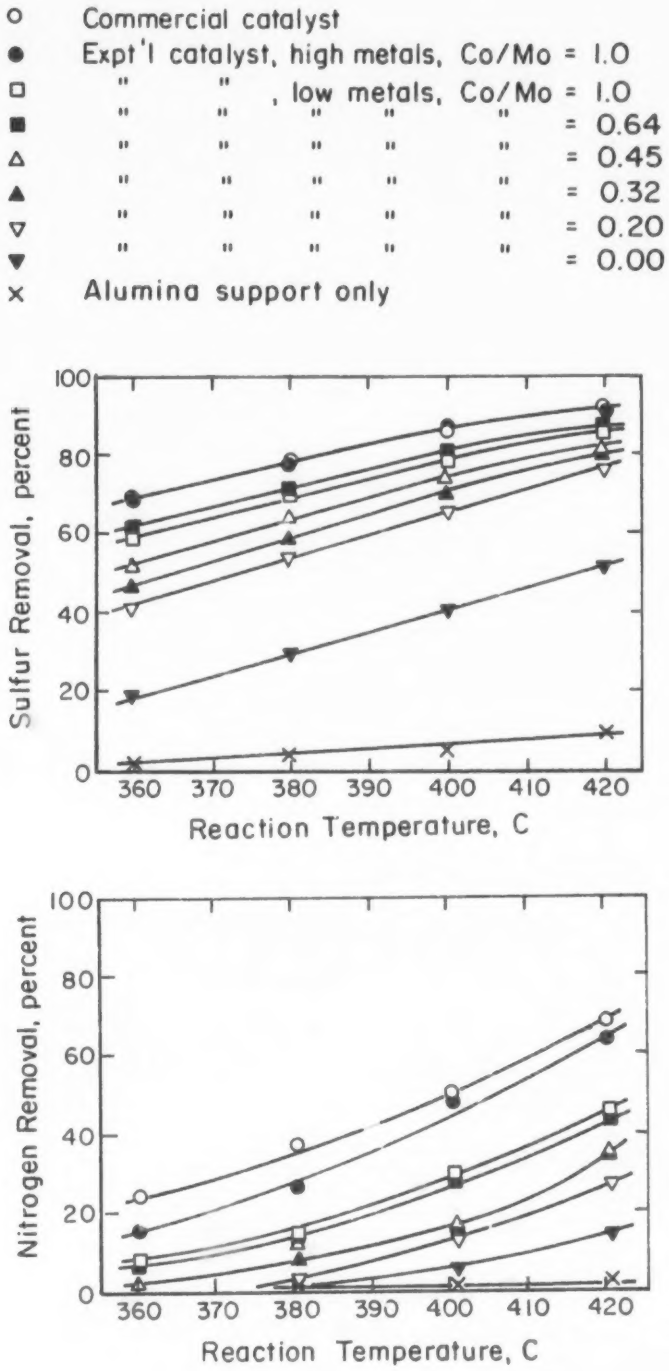


FIGURE 55. SULFUR AND NITROGEN REMOVAL IN CATALYTIC HYDROTREATING OF TAR SAND OIL(302)

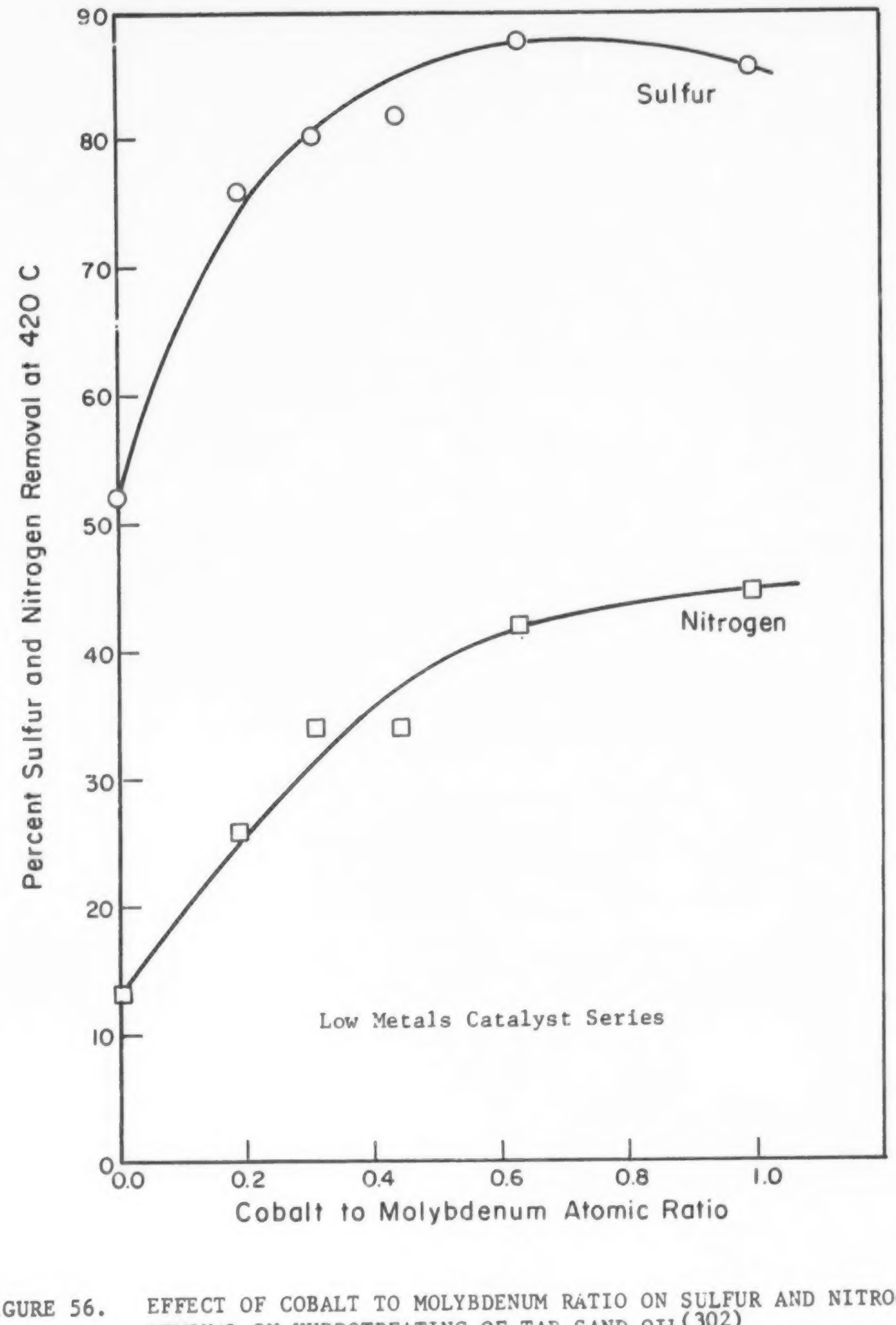


FIGURE 56. EFFECT OF COBALT TO MOLYBDENUM RATIO ON SULFUR AND NITROGEN REMOVAL IN HYDROTREATING OF TAR SAND OIL(302)

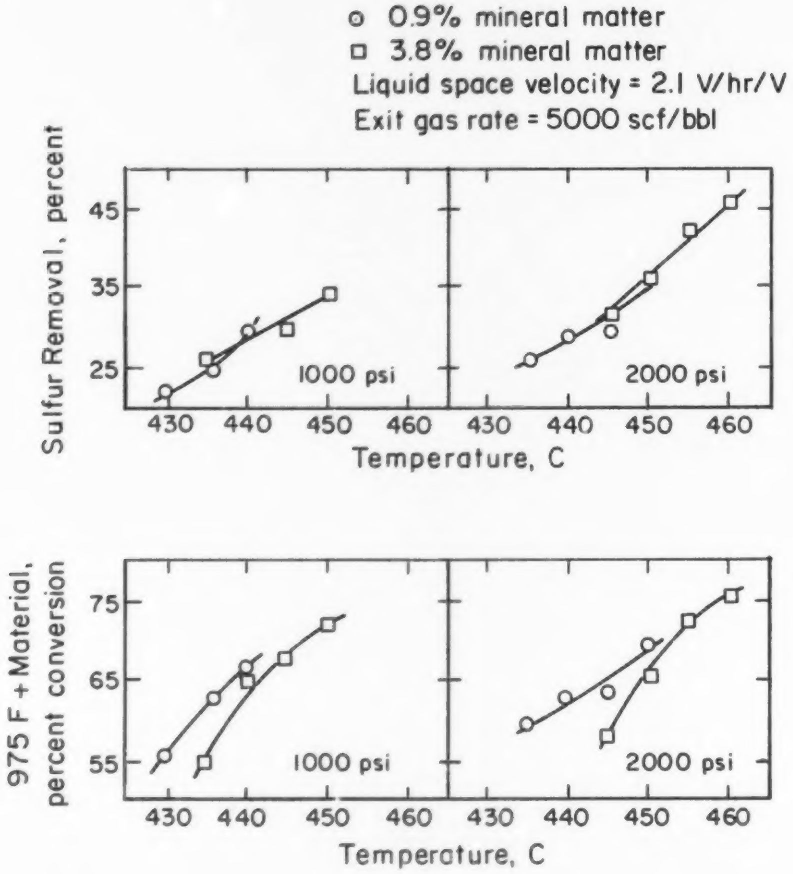


FIGURE 57. EFFECT OF MINERAL MATTER CONTENT OF TAR SAND OIL ON THERMAL HYDROTREATING(302)

Feedstock properties are given in Figure 53.

thermal hydrotreating, the severity of the operating conditions, and hence the degree of contaminant removal possible, is limited to the point at which coke and sludge begin to accumulate in the system. The data of this study indicate that the primary effect of the mineral matter is to suppress the coking and fouling reactions which limit the operating conditions. Because mineral matter does adversely affect catalytic hydrotreating, for tar sand oils with very high mineral contents thermal hydrotreating could be preferable to the catalytic process.

A modification of thermal hydrotreating which has been studied by Ternan(303) is the addition of pulverized coal as a "getter" for metals in the oil and for coke formed in the process. The coal may also have catalytic effects. Some data on this concept are given in Table 82. The operating conditions in this study were a temperature of 450 C (842 F), a pressure of 2000 psig, a hydrogen rate of 5000 scf/bbl, and a liquid space velocity of 1 $ft^3/hr/ft^3$. This study was concerned primarily with the changes occurring in the coal, and few data on the removal of contaminants from the oil were obtained. The only such data dealt with metals removal and showed that the product oil contained 16 percent less vanadium and nickel than the feed when a semianthracite coal was used and 55 percent less when a lignite was used. Since lignites have a higher porosity than other ranks of coal, they might be expected to pick up more metals from the oil. Other conclusions from this study were:

- Coal hydrogenation (to liquid and gaseous products) occurred at the conditions used.
- Petroleum-type coke was deposited on the coal particles.
- The solids remaining in the reactor decreased in mass and in particle size as the reaction progressed.
- The properties of the liquid product changed markedly as the reaction progressed.

Not all the phenomena observed are completely understood at this time. The Canadian Department of Energy, Mines and Resources is continuing its work in this interesting area.

TABLE 82. DATA ON THERMAL HYDROTREATING OF TAR SAND OIL IN THE PRESENCE OF COAL(303)

Feedstock Properties		
Sulfur, weight percent	4.72	
Nitrogen, weight percent	0.42	
V, ppm	191	
Ni, ppm	76	
Weight percent 524 C+ (975 F+)	51	
Benzene insolubles, weight percent	0.90	
Coal Properties		
Source	Canmore Cascade Area, Alberta	Estevan Saskatchewan
Rank	Semi-anthracite	Lignite
Moisture, weight percent	0.78	18.26
Ash, weight percent	7.82	10.16
Volatile matter, weight percent	13.39	35.62
Fixed carbon, weight percent	78.01	35.96
Residue Removed from Reactor		
Yield, weight percent on coal charged	94.7	47.3
Moisture, weight percent	0.70	4.99
Ash, weight percent	7.08	24.59
Volatile matter, weight percent	13.44	24.02
Fixed carbon, weight percent	78.78	46.40
Product Oil		
V, ppm	161	82
Ni, ppm	63	37
Reduction in V + Ni Content of Oil, percent	16	55
Ash in Residue as Percent of Ash in Coal Charged	86(a)	114(a)

(a) Ternan states that there are "no readily apparent explanations" for these changes in ash content.

4.2.4 Coking

Data on the coking of raw tar sand oil have been presented by Gray(304), with additional detail on the GCOS operation available from Bachman(305). These data are shown in Table 83. The GCOS operation is the only system for which the data are complete enough to analyze the contaminant removal obtained. The data indicate that about 83 percent of the sulfur in the feed remains in the liquid products plus coke, and hence the removal of sulfur (as H_2S) is only about 17 percent.

In the GCOS plant and the planned future facilities, the coke produced by the coker is used to generate steam, some of which is used directly and some of which is used to generate electricity. At the GCOS plant, the quantity of coke produced exceeds that which can be used in this manner, so some coke has been stockpiled.(305) In order to bring the coke production more in line with the needs, the future facilities are planning to use fluid coking, which produces less coke than the delayed coking process used by GCOS (see coke yields in Table 84). As mentioned previously, one of the planned facilities (Home Oil/Alminex) is to use the Flexicoking process, in which most of the coke is converted into a fuel gas. For many applications, the coke produced from tar sand oil will contain too much sulfur to permit direct combustion of it without environmental controls.

TABLE 83. DATA ON COKING OF TAR SAND OIL(304,305)

Type of Coker	Delayed	Delayed (GCOS Operation)	Fluid No Recycle	Fluid With Recycle
Data Sources	Gray	Gray, Bachman	Gray	Gray
Yields, weight percent on feed				
Gases, C_4 and lighter	8.2	8.3	8.8(a)	11.2(a)
Naphtha	15.4	12.1	8.5(a)	14.4(a)
Light gas oil	--	10.0	18.6(a)	23.4(a)
Heavy gas oil	55.0	41.4	41.4(a)	34.4(a)
Fuel oil	--	4.2	9.6(a)	--
Coke	21.0	22.7	12.3	16.0
	99.6	98.7	99.2	99.4
Weight Percent Sulfur in				
Feed		4.2		
Naphtha	1.86	2.2	1.0	1.4
Light gas oil	--	2.7	3.3	4.1
Heavy gas oil	4.04	3.8	4.8	5.4
Fuel oil	--		5.4	--
Coke		6.0(b)		
Percent of Feed Sulfur in				
Naphtha		6.3	2(c)	5(c)
Light gas oil	--	6.4	15(c)	23(c)
Heavy gas oil		37.5	47(c)	44(c)
Fuel oil	--		12(c)	--
Coke		32.4	18(d)	23(d)
		82.6	94(e)	95(e)
Weight Percent Nitrogen in				
Feed		0.36		
Naphtha		0.015	0.01	0.016
Light gas oil	--	0.040	0.06	0.08
Heavy gas oil		0.200	0.3	0.41
Percent of Feed Nitrogen in				
Naphtha		0.5	0.2(f)	0.6(f)
Light gas oil	--	1.1	3(f)	5(f)
Heavy gas oil		23.0	35(f)	39(f)

(a) Weight percent yields converted to volume percent using feed specific gravity of 1.025 (value for GCOS feed).

(b) From Synthetic Fuels Data Handbook, Cameron Engineers, Inc., p 269 (Sun Oil Co. data).

(c) Estimated using feed sulfur content of 4.2 weight percent (value for GCOS feed).

(d) Estimated using coke/feed sulfur content ratio of 6.0/4.2 = 1.43 (from GCOS case).

(e) Totals appear to be too high to reflect probable sulfur in gases, thus indicating uncertainties in estimating procedures.

(f) Estimated using feed nitrogen content of 0.36 weight percent (value for GCOS feed).

4.3 Shale Oil

4.3.1 Differences from Petroleum

The source of shale oil is the "kerogen" (molecular weight > 3000) found in oil-shale rock. Depending on retorting conditions, the high-molecular-weight polycyclic aromatic compounds in the kerogen are converted to shale oil. The bulk of the carbon in the shale oil produced by present technology has three to four aromatic ring structures, and shale-oil fractions typically contain only 3 to 8 percent paraffins. The shale oil is highly aromatic in nature compared with petroleum. Consequently, essentially all the sulfur and nitrogen contaminants occur in heterocyclic structures. The sulfur content of shale oil is lower than that of most petroleum crudes, but the nitrogen content is much higher than that of petroleum.

4.3.2 Adsorption

Burger(306) has studied the use of various adsorbents for removing arsenic from shale-oil fractions. The fractions studied contained 10 to 60 ppm of arsenic. "Moderate success" was reported for silica gel, sulfuric acid on silica gel, hydrogen peroxide on silica gel, caustic on silica gel, activated alumina, and activated carbon. The relatively high concentration of arsenic in shale oil makes its removal considerably more difficult than that from petroleum. A number of studies were conducted in the mid-1950's to early 1960's on removing arsenic from petroleum naphtha fractions, but these fractions contained less than 0.4 ppm of arsenic. A review of this work is given by Burger.

4.3.3 Hydrotreating

A considerable amount of experimental work has been done on catalytic hydrotreating of raw shale oil and shale-oil fractions. Because the objective in hydrotreating shale oil is primarily to remove nitrogen, which is harder to remove than sulfur, the conditions are generally more severe than in most petroleum hydrotreating operations. The operating pressures and the hydrogen consumptions are relatively high. One factor tending to make the hydrogen consumption greater for shale oil than for petroleum is that shale oil contains more olefins, and these are saturated during hydrotreating. Catalyst-poisoning problems due to metals, such as arsenic, are more severe for shale oil than for most types of petroleum.

Some typical data on the hydrotreating of raw shale oil are shown in Table 84.(307) As the operating pressure is increased, the sulfur and nitrogen removals increase, the hydrogen consumption increases, and the coke production decreases. Note that at conditions at which 90 percent of the sulfur is removed, only about 51 percent of the nitrogen is removed. Nitrogen removals of over 90 percent can be obtained if the operating pressure is high enough.

Some additional data from the same laboratory are shown in Figure 58.(308) The nitrogen removal is shown as a function of space velocity and pressure. The data from this study indicated that the hydrogen partial pressure has a significantly greater effect on the denitrogenation rates of indole-type nitrogen compounds than on those of quinoline-type compounds. At low pressures and temperatures the denitrogenation rate constants for quinoline-type compounds are greater than those for indole-type compounds, whereas the reverse is true at higher pressures and temperatures.(309) The latter portion of this statement is in agreement with a previous study at very high pressures (5000 psi).(308) In the high-pressure study, it was concluded that the denitrogenation of the predominantly aromatic-type nitrogen compounds in shale oil takes place by the following three steps:

(1) Hydrogenation of the nitrogen-containing rings

(2) Rupture of the saturated rings to form amines

(3) Decomposition of the amines to form ammonia.(308)

Flinn(310) has conducted exploratory studies on the vapor-phase hydrotreating of shale oil immediately following retorting in the presence of hydrogen. A bed of cobalt-molybdate catalyst was placed behind a bed of crushed oil shale, and hydrogen was passed through the

TABLE 84. DATA ON HYDROTREATING OF RAW SHALE OIL(307)

Green River Shale Oil (0.68% S, 2.18% N)
Cobalt-Molybdenum Catalyst

Operating Conditions(a)				
Pressure, psig	500	1,000	1,500	3,000
Average temperature, C (F)	477 (890)	475 (887)	473 (883)	473 (884)
Hydrogen Consumption, scf/bbl	1,030	1,650	1,890	2,500
Yields, weight percent on feed(b)				
H_2S	0.65	0.69	0.70	0.71
NH_3	1.35	2.22	2.52	2.63
C_1-C_3	7.15	10.19	10.26	9.93
C_4 + gasoline	28.91	37.17	43.78	53.31
Fuel oil	58.57	48.75	42.71	35.25
Coke on catalyst	3.03	1.58	1.06	0.23
Percent of Feed Sulfur in				
H_2S	90.0	95.5	96.9	98.3
C_4 + gasoline	2.1	0.5	0.6	0.8
Fuel oil	7.8	2.2	2.5	0.5
Percent of Feed Nitrogen in				
NH_3	50.9	83.8	95.1	99.2
C_4+ gasoline	11.8(c)	4.8(c)	0.8	0.2
Fuel oil	37.3(c)	11.4(c)	3.9	0.6
Weight Percent Nitrogen in				
C_4 + gasoline	0.89	0.28	0.04	0.01
Fuel oil	1.47	0.54	0.20	0.04

(a) Conditions also include liquid hourly space velocity = 1.0, hydrogen circulation rate = 6000 scf/bbl.

(b) Yields on feed total more than 100 percent because of hydrogen added.

(c) By difference from 100 percent. Nitrogen balance was in error by 1 to 2 percent.

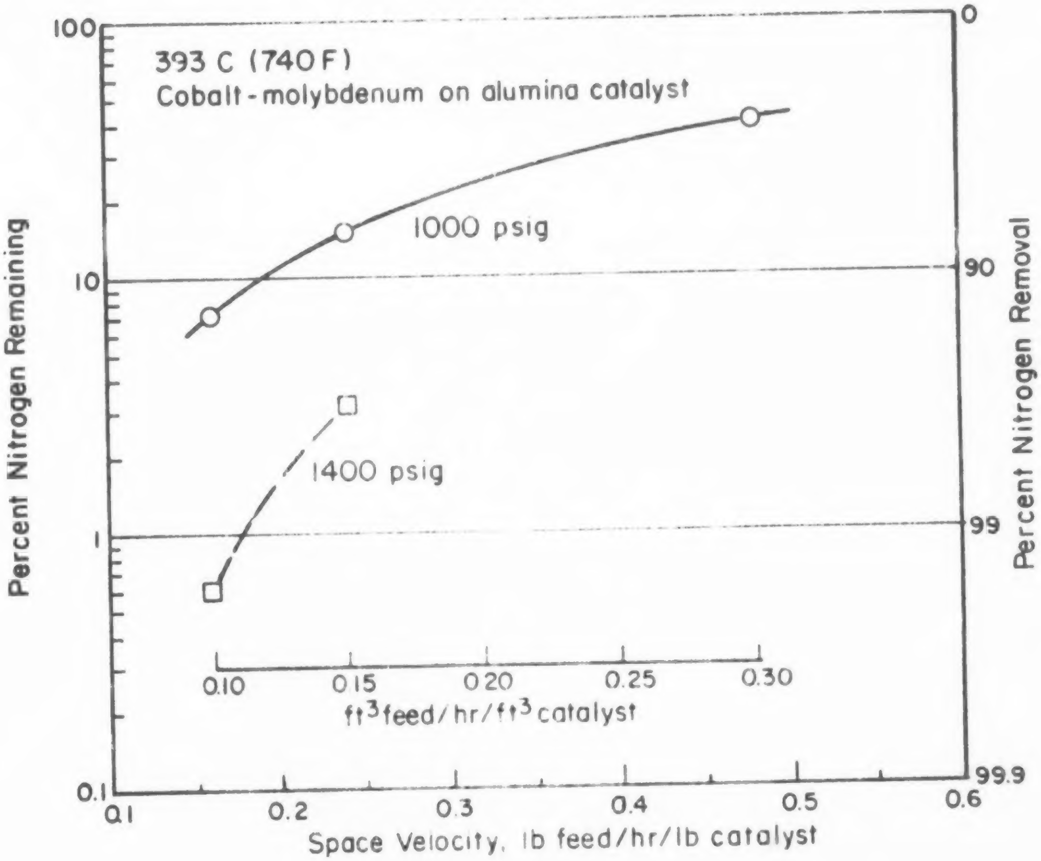


FIGURE 58. NITROGEN REMOVAL IN HYDROTREATING OF SHALE OIL(308)

bed. The reaction temperatures were 425 to 450 C (800 to 850 F) and the pressures were 150 to 550 psia. The product oil from the retorting plus hydrotreating operation contained <0.07 weight percent nitrogen and <0.04 weight percent sulfur. Without the catalyst (i.e., retorting only), the concentrations were 1.3 to 2.2 percent nitrogen and 0.3 to 0.4 percent sulfur.

4.3.4 Sulfuric Acid Treatment

Burger(306) tested the use of sulfuric acid washing for removing arsenic from shale-oil fractions and found it "ineffective" for that purpose. The shale-oil fractions studied contained 10 to 60 ppm of arsenic.

On the other hand, a combination of sulfuric acid washing and caustic washing has been found effective for removing nitrogen from shale oil. Poulson(311) reports the following results for treatment of a light gas oil fraction (204 to 354 C or 400 to 670 F) of a shale oil. The treatment consisted of successive contacting at a temperature of 38 C (100 F) with 15 weight percent NaOH, 20 weight percent H_2SO_4, and 100 percent H_2SO_4 (22.8 lb/bbl oil), then neutralization with 3 volume percent NaOH and redistillation to restore the end point. The result was a reduction of the nitrogen content of the oil from 1.66 weight percent to 0.085 weight percent. The sulfur content was nearly unaffected, being reduced only from 0.84 weight percent to 0.74 weight percent. The yield of product was only 67 volume percent on feed, which represents a drawback to this treatment procedure. Poulson generalizes by stating that, "Undoubtedly quite effective nitrogen and oxygen compound removal could be achieved with various reactants or solvents, but it is unlikely that improvement in sulfur level would be obtained because of the chemical similarity of thiophene-type compounds to the hydrocarbon matrix".(311)

4.3.5 Caustic Alkali Treatment

Burger(306) reports "fairly substantial" removal of arsenic from shale-oil fractions by washing with aqueous caustic (NaOH) solutions.

After a number of batch extraction experiments, a 75-hour continuous test was run with recycle of the caustic phase. The feedstock for this run was a 204 to 454 C (400 to 850 F) shale-oil fraction containing 40 ppm of arsenic. The NaOH concentration of the initial charge and the makeup of caustic was 15 weight percent. The extraction temperature was 177 C (350 F) and extractor residence time was 30 minutes. The weight ratio of oil feed to total caustic feed to the extractor was 6.3. The weight ratio of oil feed to fresh caustic makeup was 100 for most of the run but was 200 for the last 13 hours of the run. The arsenic content of the product oil was about 12 ppm, which corresponds to about 70 percent arsenic removal. The oil lost to the caustic phase was less than 0.5 percent of the oil feed.

4.3.6 Coking

Coking of raw shale oil is frequently mentioned as a possible first step in refining the oil. One reason for this is that raw shale oil normally contains a small amount of fine solid material carried over from the retorting operation, and this solid material will be removed with the coke produced. When using this option, the intention is to follow the initial coking operation with additional processing (presumably hydrotreating) of the liquid products to remove nitrogen and sulfur.

The Bureau of Mines(312) has obtained some data on the coking of raw shale oil, and these data are given in Table 85. Although the nitrogen and sulfur balances do not close as well as one might like, one can see that about 77 percent of the nitrogen and 74 percent of the sulfur in the feed remain in the liquid products. Even if the material-balance error is attributed entirely to the gas phase, the overall removals (to gaseous species) of nitrogen and sulfur are only 13 percent and 24 percent, respectively. This level of sulfur removal generally agrees with the level given for petroleum in the preceding section.

TABLE 85. DATA ON ONCE-THROUGH DELAYED COKING OF RAW SHALE OIL(312)

Nevada-Texas-Utah Shale Oil

	Operating Conditions	
	Temperature, C (F)	Pressure, psig
Heater outlet	504 (940)	150
Top of coke chamber	416 (780)	24

Stream	Yield, weight percent on feed	Weight Percent N	Percent of Feed N	Weight Percent S	Percent of Feed S
Feed		2.20		0.92	
Gas	3.1	1.07	1.5	4.59	15.5
Naphtha	13.3	0.98	5.9	0.92	13.3
Light gas oil	30.5	1.70	23.6	0.80	26.5
Heavy gas oil	47.6	2.20	47.6	0.66	34.1
Coke	4.8	4.4	9.6	0.5	2.6
Loss	0.7				
Total	100.0		88.2		92.0

4.3.7 Gasification

Shale oil obtained by retorting can be gasified in the same manner as petroleum. However, the work to date has been directed at hydrogasification, i.e., gasification in the presence of hydrogen. The Bureau of Mines(313) has studied the hydrogasification of raw shale oil (Green River Formation) over a cobalt-molybdenum catalyst. This catalytic operation may be regarded as a combination of hydrotreating and gasification. The operating conditions included temperatures ranging from 427 to 704 C (800 to 1300 F) and pressures of 500, 1000, and 1500 psig.

Another option is possible for shale, and that is a conversion of the mined oil shale directly into gas, thus combining the retorting and gasification steps. This alternative has been studied by the Institute of Gas Technology, which refers to its process as a hydrogasification of oil shale.

A flow sheet for the IGT process is presented in Figure 59.(314) A three-zone retorting/gasification reactor is used. A hydrogen stream, flowing countercurrently to the shale, recovers heat from the reacted shale in the bottom zone and, bypassing the middle zone, transfers the heat to the fresh shale in the top zone. A separate, heated hydrogen stream, flowing either cocurrently or countercurrently, reacts with the shale in the middle zone. The major portion of the kerogen conversion occurs in the middle zone. The purpose of the three-zone reactor is to obtain the efficiency of countercurrent heat utilization without product condensation and related plugging problems.(314)

In tests, up to 60 percent of the organic carbon in the oil shale has been converted to gas or up to 80 percent has been converted to liquid products boiling below 400 C. When a mixture of gas and liquid products is produced, the overall conversion of organic carbon into products is up to 95 percent.(315) Thus, when the process is run for maximum gasification, up to 35 percent of the feed is still converted into liquid products.

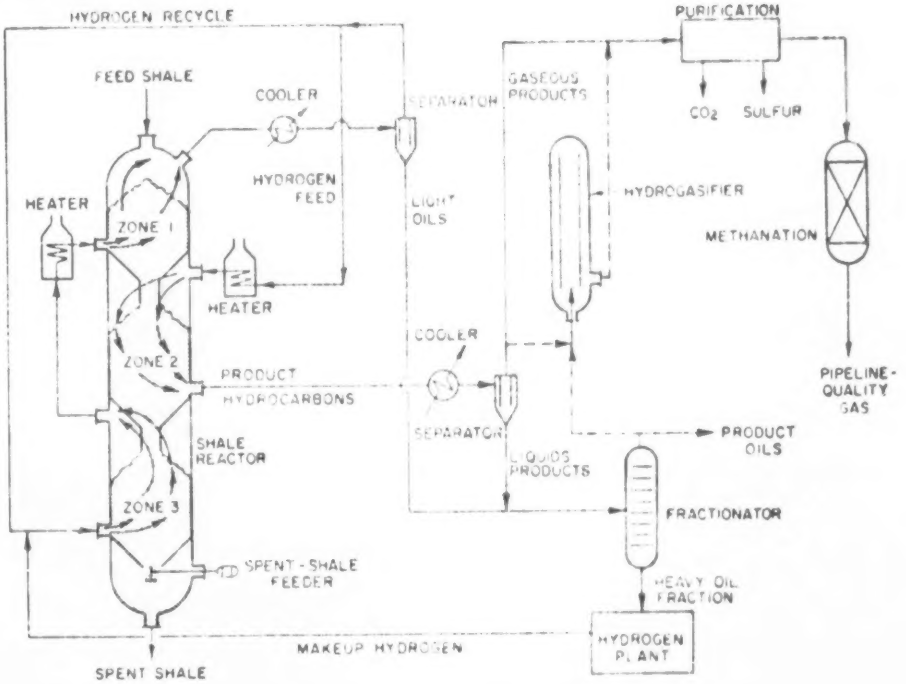

HYDROGEN RECYCLE
FEED SHALE
COOLER
SEPARATOR
GASEOUS PRODUCTS
PURIFICATION
CO_2
SULFUR
HYDROGEN FEED
LIGHT OILS
HEATER
ZONE 1
HEATER
HYDROGASIFIER
METHANATION
COOLER
ZONE 2
PRODUCT HYDROCARBONS
SEPARATOR
PIPELINE-QUALITY GAS
PRODUCT OILS
SHALE REACTOR
LIQUIDS PRODUCTS
ZONE 3
FRACTIONATOR
SPENT-SHALE FEEDER
HEAVY OIL FRACTION
MAKEUP HYDROGEN
HYDROGEN PLANT
SPENT SHALE

FIGURE 59. FLOW SHEET FOR IGT OIL SHALE HYDROGASIFICATION PROCESS(314)

No published data have been found on the nitrogen and sulfur content of the liquid products, but sources familiar with the work indicate that these products are very clean.

4.4 Summary of Removal Methods

A summary of the general effectiveness of the contaminant-removal methods for tar sand oil is presented in Table 86. Only hydrotreating and conversion processes have been used but the lack of data on nitrogen and trace element removal prevent determination of their overall effectiveness for the removal of all three types of contaminants (sulfur, nitrogen, and trace elements).

A summary of the general effectiveness of the removal of contaminants from shale oil is presented in Table 87. As was true for petroleum, hydrotreating and gasification are the only known methods with the potential for effectively removing all the contaminants (sulfur, nitrogen, and trace elements) from shale oil.

TABLE 86. METHODS OF REMOVING CONTAMINANTS FROM TAR SAND OIL

		Contaminant Removal(a)		
	Removal Method	Sulfur	Nitrogen	Trace Elements
II.	Hydrotreating			
	Catalytic	+		
	Thermal	+(b)		
	Thermal with coal addition			+(c)
III.	Conversion Processes			
	Noncatalytic processes	+(d)		

(a) Plus (+) = all or part (normally >50 percent); negative (-) = negligible removal.

(b) Data available showed 45 percent sulfur removal.

(c) Data available showed 55 percent metals removal with lignite, 16 percent with semianthracite coal.

(d) Data available on coking process showed 17 percent sulfur removal.

TABLE 87. METHODS OF REMOVING CONTAMINANTS FROM SHALE OIL

Removal Method	Contaminant Removal(a) Sulfur	Contaminant Removal(a) Nitrogen	Contaminant Removal(a) Trace Elements
I. Physical Methods			
Adsorption			+(b)
II. Hydrotreating	+	+	
III. Chemical Refining			
Sulfuric acid treatment	-(c)	+(c)	-(b)
Caustic treatment		+(c)	+(b)
IV. Conversion Processes			
Noncatalytic processes	+(d)	-(d)	
V. Gasification	+	+	+

(a) Plus (+) = all or part (normally >50 percent): negative (-) = negligible removal.

(b) Only arsenic was studied. Quantitative data are not given except for caustic treatment (70 percent arsenic removal).

(c) Specific combination of sulfuric acid treatments and caustic treatments gave >90 percent nitrogen removal, <15 percent sulfur removal.

(d) Coking process gives 20 to 30 percent sulfur removal. <15 percent nitrogen removal.

5.0 TECHNICAL SUMMARY AND CONCLUSIONS

In the first volume of this study, the contaminants in coal, petroleum, tar sand oil, and shale oil were categorized as those being present as discrete phases and those being part of the fuel structure (carbon skeleton) of the host fuel. In the case of coal, those contaminants present as discrete phases could in effect be released during size reduction of the coal and then separated from the coal by differences in physical properties between the noncombustible contaminant phases (pyrites and other mineral matter) and the coal. The removal of those contaminants present in the coal as part of the carbon skeletal structure (i.e., primarily as organic sulfur and organic nitrogen compounds) would require disruption of the molecules to cause the release of the sulfur and nitrogen through bond cleavage. Such approaches require severe reaction conditions which may or may not be selective for removal of the contaminants.

In the case of the petroleum, tar sand oil, and shale oil, similar conclusions might be reached. The amount of mineral matter present as discrete phases is very much less in these liquid fuels than in coal. The sulfur, nitrogen, and trace elements in liquid fuels must be removed by chemical reaction because they are part of the fuel structure. As an alternative, the contaminants may be concentrated in the residue left after distillation of cleaner fuel from the crude fuel. When this is done, part of the fuel value becomes a heavily contaminated material that is difficult to utilize in an environmentally acceptable way. When liquefied coal is distilled, similar concentration of the contaminants in the residues (chars) occurs. Tar and oils and shale oils when utilized as refinery feed stock would undergo similar redistribution of the contaminants they contained.

5.1 Contaminant Removal From Coal

Raw coal, which contains large amounts of undesirable mineral matter, undergoes considerable upgrading in modern coal-preparation operations. Significant amounts of sulfur present as gross pyrite inclusion and other ash mineral bodies present in the mined coal are readily removed during coal-washing operations. When such processes are used, 15 to 30 percent of the pyritic sulfur in the run-of-the-mine coal is removed from coal crushed to a top size of 1/4 inch. Partial removal of finely disseminated pyrite by physical means can be accomplished only if the size of the coal is further reduced. In separations using the dense media cyclone, a bottom size of 32 mesh can be treated to remove up to 30 percent of the pyrite. By employing froth flotation, pyrite removal can reach about 50 percent when the coal is crushed to minus 28 mesh. Staged froth flotation employing pyrite depressants in the second stage reduce the pyritic sulfur content of coals anywhere from 50 to 80 percent. Specialized methods for pyrite removal from coal that has been reduced in size to minus 200 mesh and even minus 325 mesh have had varying success. Typically, removal of 40 to 50 percent of the pyritic sulfur can be attained. In one case in which an oil agglomeration technique was used, the amount of pyrite removal reached 90 percent. However, special precondition of the minus 325-mesh coal was needed.

In chemical refining, essentially all of the pyritic sulfur in coal is reported to be removed by treatment with aqueous solutions of sodium hydroxide or ferric sulfate. Both processes require elevated temperature. With sodium hydroxide partial removal of organic sulfur seems to occur for selected coals, while ferric sulfate treatment does not attack it. In both these processes more efficient removal of pyrite occurs when finer sized coal is treated.

Liquefaction or depolymerization of coal to produce a cleaner solid fuel, as in the case of solvent-refined coal (SRC), is an alternative to the extensive size reduction of coal needed to gain access to the finely disseminated pyrite and mineral matter. During such a liquefaction, noncatalytic hydrogenation of coal occurs mostly from the hydrogen-donor type solvent that is mixed with the coal. After the liquefaction, the mineral matter and the finely disseminated pyrite (now reduced to pyrrhotite or ferrous sulfide) originally in coal are released. They along with unreacted coal are removed prior to utilization. Typically, nearly all of the ash minerals are removed and the sulfur is lowered to values equal to or less than that attributable to organic sulfur in coal. Nitrogen values are usually not lowered in such a process. Most of the cyclic and heterocyclic organic sulfur and organic nitrogen originally present in the coal remain as such in this type of liquefaction product (SRC). Further removal of this sulfur and nitrogen must be done by catalytic hydrotreatment of the liquefaction product to release most of the sulfur as H_2S and part of the nitrogen as NH_3.

Desulfurization and denitrification of coal by carbonization or pyrolysis are only partially effective since, during the processing, the sulfur and nitrogen not removed overhead remain in the coke or char in a form that is bound deeply in graphitic-type structures. Processes employing reactive gases, alkalies, salts, and acids during carbonization or pyrolysis are capable of increasing the amount of sulfur and nitrogen removed, but complete removal has not been attained. Unless the coal used in these processes is low in ash and pyrite by virtue of their origin or coal preparation, most of these components will remain in the coke or char.

The gasification of the carbon value in coal releases the sulfur and nitrogen bound in the coal structure as well as those present as discrete phases. However, before the low-Btu gas can be utilized, these released gaseous contaminants and the particulates must be removed downstream from the gasifier. Although at first hand such an approach would appear to be an effective way to remove the contaminants from coal, the solid fuel is usually converted in the process to a low-grade gaseous fuel.

5.1.1 Conclusions

It may be concluded from these facts on the removal of contaminants from coal that:

- Release from coal of the finely disseminated pyrite requires extensive size reduction of the coal before even partial removal of the pyritic sulfur can be accomplished. This is true whether the pyrite-removal method is based on chemical refining or on differences in specific gravity, surfacial behavior, or magnetic properties.
- Only about one-half of the sulfur originally present in coal as pyrite is removed during liquefaction or depolymerization of coal by noncatalytic hydrogenation. The product (pyrrhotite or FeS) must be removed before it can be utilized as a low-sulfur fuel.

- The sulfur and nitrogen present as cyclic and heterocyclic organic sulfur and organic nitrogen are relatively unaltered by either the physical methods or chemical refining and only a small amount of the organic sulfur is released during the noncatalytic liquefaction process.
- Carbonization of coal is only partially effective for the removal of the sulfur and nitrogen contaminants. Those that remain in the product are tied up in the char structure.
- Gasification of coal releases all of the contaminants contained in coal, but extensive posttreatment of the gasified coal to remove gaseous and particulate pollutants is required before the gas can be utilized.

5.2 Contaminant Removal From Liquid Fuels

The liquid fuels--petroleum, tar sand oil, and shale oil--contain small amounts of gaseous contaminants, namely H_2S and NH_3, which can be removed by a wide variety of processes, including a simple stripping operation. Petroleum often contains some water-soluble salts, primarily NaCl, which are readily removed by water washing. Relatively simple organic sulfur contaminants, such as mercaptans and some organic sulfates, can be removed by treating the oil with acids (usually H_2SO_4) or bases (usually NaOH). Removal of sulfur and nitrogen which are bound in more complex organic molecules requires more severe treatments. Nitrogen is generally more difficult to remove than sulfur. Hydrotreating is relatively effective in removing sulfur and nitrogen contaminants, although it significantly changes many properties of the fuel. Hydrotreating may not be economical or practical for very heavy, high-metals-content oils, and often only the lighter distillates are hydrotreated to remove sulfur as H_2S and nitrogen as NH_3. Metals can be removed from fuels by an irreversible deposition of the metals on a catalyst-like solid at moderate temperatures. Ability to remove metals prior to hydrotreatment increases the amount and the types of liquid fuels that might be processed.

The processes which are used to convert heavy liquid fuels into lighter fuels are relatively ineffective in removing contaminants from the overall fuel but, instead, tend to concentrate them into the heavier fraction. The catalytic conversion processes, such as catalytic cracking, are often not economical or practical for very heavy, high-metals-content oils. The noncatalytic conversion processes, such as coking, are generally applicable but are particularly ineffective in removing contaminants.

Coal liquids formed during the initial stages of the hydrogenation of coal contain the noncombustible portion and unreacted coal as slurry materials, and they also contain most of the contaminants originally present in the coal. At this point in processing, several alternative approaches for the removal of contaminants become available. As one alternative, the removal of the mineral matter, unreacted coal, and iron sulfide as in the solvent-refined coal (SRC), will provide a product fuel which is reduced in ash and total sulfur and a solid at ambient temperatures. This same product can be used as a feedstock for a catalytic hydrotreatment process. Another alternative is to catalytically hydrogenate a coal-oil slurry to produce a liquid fuel (i.e., liquid at ambient temperatures) and then remove the suspended solids. During this catalytic hydrogenation, much of the organic sulfur and part of the organic nitrogen is removed. Still another alternative is to leave the solids in the liquid after hydrotreatment, and distill the product fuel and leave the insoluble material in the residue (as well as some of the sulfur and nitrogen that is more difficult to remove). Other variations of the process exist, but these alternatives appear to be most common.

To accomplish nearly complete removal of the organic sources of sulfur and nitrogen requires exhaustive hydrogenation using amounts of hydrogen well in excess of that equivalent to the contaminants being removed. This poor overall hydrogen utilization exists because the contaminant-removal reaction occurs concurrent with hydrogenation of the coal, which produces less desirable hydrocarbons and light fractions mixed with H_2S and NH_3.

Even though it is done frequently, the concentrations of sulfur, nitrogen, and trace elements in the coal liquid products probably should not be used as a measure of the effectiveness of the overall contaminant-removal method, since the final liquid products have different processing histories. The fraction of the coal recovered as an environmentally acceptable fuel should also be given consideration in the comparisons.

5.2.1 Conclusions

From this summary of the removal of contaminants from liquid fuels, it may be concluded that:

- Simple organic sulfur contaminants present in petroleum but less likely to be found in the other liquid fuels can be removed by chemical treatment.
- More complex organic sulfur and organic nitrogen molecules existing in the liquid fuels and coal liquids can be removed by catalytic hydrotreatment to form H_2S and NH_3.
- Metals in petroleum and the other liquid fuels interfere with catalytic hydrotreatment and must be absent or in very low concentration before such treatment is undertaken.
- Conversion processes in which lighter liquids are recovered from heavy liquid fuels are relatively ineffective for contaminant removal.
- Hydrotreatment reactions change many of the properties of the fuel as well as removing sulfur as H_2S and nitrogen as NH_3.

5.3 Interrelational Aspects of Contaminant Removal

An obvious interrelationship exists between the commercial coal-preparation processes used to remove contaminants from run-of-the-mine coal and the need for quality coal feedstock used in other types of contaminant-removal processes. The processes based on liquefaction, chemical refining, pyrolysis, other types of physical methods, and gasification attempt to remove contaminants that usually can be removed only partially or are impossible to remove by the combined commercial preparation processes (i.e., grinding, washing, dense-media separation and froth flotation). The limit to which the size of the coal can be ground to optimize processing cost and minimize fuel losses during the coal preparation also influences the extent of removal of contaminants. However, when feed coal is to be prepared in such a facility for utilization in, for example, chemical refining, trade-offs would have to be made between coal losses and maximum removal of reagent-consuming contaminants prior to chemical processing.

In any study on the removal of contaminants from solid and liquid fuels, it is necessary to consider how the removal of one class or type of contaminant affects concurrent or subsequent removal of another class or type of contaminant. For example, liquefaction by catalytic hydrogenation removes the organic sulfur, some organic nitrogen, and half of the pyritic sulfur (FeS_2 is converted to FeS) as H_2S. However, the removal of ash minerals from the liquid fuel is a costly and difficult step. If the coal were subjected to a cleaning process for removing pyrite (physical separation or chemical refining) prior to catalytic hydrogenation, it may not be necessary to separate the ash from the liquid fuel after catalytic hydrogenation. The resultant low-sulfur but ash-containing fuel would probably be suitable for power plant and industrial boiler applications. Such combined processes can best be illustrated by examples cited in the literature.

Meyers, Hamersmas, et al.(316) have investigated, on a laboratory scale, the combination of chemical refining (Meyers process using ferric sulfate) with coal liquefaction in order to ascertain the viability of such a combined process. The filtration step that normally follows liquefaction of coal was eliminated by, first, leaching with ferric ion to remove 93 to 98 percent of the pyritic sulfur and, second, hydrogenation to remove 57 to 59 percent of the organic sulfur as hydrogen sulfide. The product fuels contained the normal coal ash content less the pyrite which was removed. It was suggested that the ash component of the fuel could be removed by available post-combustion emission-control techniques. Without first chemical refining, it was found that about 50 percent of the pyritic sulfur remained as iron sulfide after hydrogenation. The authors concluded from their data on the treatment of coals from two different beds that the combined process is technically feasible for the desulfurization of coal to meet control standards. They also suggested that the iron sulfate and elemental sulfur removal steps of the Meyers process might be deferred to the hydrogenation step to further simplify the combined processes because of the observed elimination of sulfate during hydrogenation and the known high reactivity of elemental sulfur.

Another aspect of the separation of iron sulfide formed during liquefaction of coal by hydrogenation has been reported by Lin, et al.(317) The authors have investigated the use of high-gradient magnetic-separation technique for the removal of the reduced pyrite (pyrrhotite) and ash components from a coal liquid (SRC) filter feed slurry. Reductions of the total sulfur and ash content have been as great as 70 and 76 percent, respectively. These studies have been performed in bench-scale experiments.

The same authors(317) have also shown that removal of the magnetic components (mostly pyrite) from raw coal (ground for SRC feed) prior to hydrogenation significantly alters the rate of liquefaction of the coal yet does not influence the organic hydrodesulfurization rate. Lin, et al.,(317) concluded that, when most of the pyrite and other minerals were removed magnetically prior to liquefaction, hydrogenation of the coal was held to a minimum for a fixed amount of hydrodesulfurization. Hence, the removal of mineral matter prior to liquefaction may be advantageous for efficient hydrogen utilization. The authors are examining trade-offs between magnetic separation prior to and after liquefaction.

Another example of the interrelation between fuel contaminants is the desulfurization of crude oil. The major difficulty has been the tendency to poison catalysts by deposition of heavy metals such as nickel and vanadium. Technology is available to remove the metals from the residual oil fraction so that the desulfurization catalyst, which is used in a subsequent operation, would not be rapidly poisoned. Demetallization technology is relatively expensive because the reaction proceeds quite slowly over naturally occurring catalysts. An alternative procedure is to remove the heavy gas oil fraction, which normally contains only trace quantities of catalyst poisons, from the crude oil by vacuum distillation and to desulfurize this fraction. However, a large amount of sulfur-containing residual oil is left which is difficult to utilize in an environmentally acceptable manner.

Solvent deasphalting had been used as an alternative to distillation to reduce the effect of the heavy metals and concentrate them and the sulfur in the asphaltene fraction. This technique has been replaced by the more advanced distillation approaches. Because of the inherently high levels of asphaltenes present in coal liquids, the use of solvent deasphalting may prove beneficial. Such treatment would concentrate the nitrogen and sulfur contaminants, which require severe hydrogenation conditions for desulfurization and denitrification, into an insoluble fraction. Hydrotreatment of this fraction would permit an efficient use of hydrogen for the removal of sulfur and nitrogen rather than hydrogenation of the hydrocarbons of the coal liquid.

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